

# Highly Z-stereoselective synthesis of 1,3-oxathiol-2-ylidenes and 4-methylene-oxazolidine-2-thiones through atom selective 5-exo-dig cyclization of propargyl alcohol with isothiocyanate

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## Supporting Information

**ABSTRACT:** DBU mediated 5-exo-dig cyclization of isothiocyanate and propargyl alcohol leading to

valuable heterocyclic compounds has been accomplished. Different mode of nucleophilicity

(either S-selective or N-selective) of isothiocyanates

was found to depend on the substitution pattern of

propargyl alcohol. The terminal propargyl alcohol and

isothiocyanate underwent N-nucleophilic attack to afford 3-substituted 4-methylene oxazolidine-2-thiones.

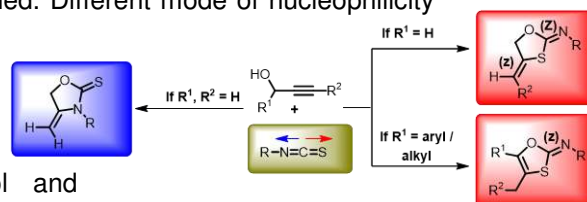
On contrary, exclusive S-nucleophilic cyclization was observed with internal propargyl alcohol to produce

(Z)-1,3-oxathiol-2-ylidenes and (Z)-N-(Z)-4-ethylidene-1,3-oxathiolan-2-ylidenes from secondary and

primary propargyl alcohol, respectively. The formation of high Z-selectivity in imine motif and alkene is the

highlight of this new method, the former is due to electronic factors and the later is because of steric

factors.

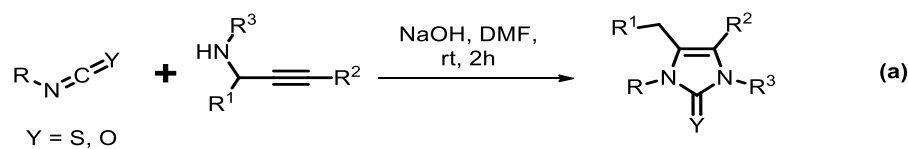


**INTRODUCTION:** 1,3-oxathiol-2-ylidenes having exocyclic imine and exocyclic C=C bond is an interesting class of heterocyclic compounds with significant biological activities<sup>1</sup> yet its synthetic routes

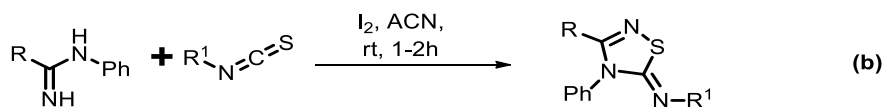
are still limited.<sup>2</sup> On contrary, oxazolidine-2-thione units are commonly found in natural products and pharmaceuticals with wide ranging bioactivities.<sup>3-4</sup> Due to their biological significance and limited number of synthetic routes, developing an efficient method towards 1,3-oxathiol-2-ylidenes and oxazolidine-2-thione derivatives<sup>5</sup> with good geometrical selectivity is a matter of interest. In general, the selectivity around C=C bond is well known and governed by either electronic or steric factors. On the other hand, the selectivity around C=N bond is somewhat rare and less studied area. Importantly, the multiple selectivities around C=X bond (X= C,N) in a single system would be highly challenging and indeed hard to achieve. The synthetic method with such selectivity would play significant role in all fields of chemistry.

In recent years, propargyl alcohol has emerged as a prolific synthon of broad synthetic utility in the context of heterocyclic compounds<sup>6</sup> and many more interesting organic transformation.<sup>7</sup> Strategy for substituted pyrroles and pyridines from propargyl alcohols with terminal alkyne under transition metal catalyzed condition is well established.<sup>8</sup> Propargyl alcohol is also known to react with sulphur dioxide leading to oxathiolene oxide<sup>9</sup> while reacting with carbon dioxide it affords cyclic carbonates under transition metal catalyzed condition.<sup>10</sup> Isothiocyanates, being a higher congener of carbon dioxide are expected to be more reactive than carbon dioxide and thus found numerous application in synthesis of heterocyclic compounds.<sup>11</sup> More interestingly, isothiocyanates are equipped with multiple reaction centers, i.e, one electrophilic centre at carbon and two nucleophilic centers at nitrogen and sulphur. Therefore, different mode of nucleophilic attack by isothiocyanates is almost inevitable under different reaction conditions and with different substrate with which it reacts. The –NCS group predominantly involved in resonance hybrid and so it reacts through either C=S or the C=N bond. The literature precedence is also in agreement that different circumstances will determine whether nitrogen or sulphur atom to act as a nucleophile of isothiocyanate molecule.<sup>12</sup> Dethe *et al* demonstrated that propargyl amine reacts with isothiocyanates under basic condition to produce imidazole-2-thiones and spirocyclic imidazolidine-2-thiones by triggering N-nucleophile (Scheme 1a).<sup>13a</sup> In a different instance, Nakka *et al* reported that S-nucleophile based cyclization of 2-aminopyridine/amidine with isothiacyanates via N-S bond formation for the synthesis of N-fused and 3,4-disubstituted 5-imino-1,2,4-thiadiazoles (Scheme 1b).<sup>13b</sup> Thus, the mode of nucleophilic attack of isothiocyanate varies and mainly governed by reaction conditions and the reacting partners.

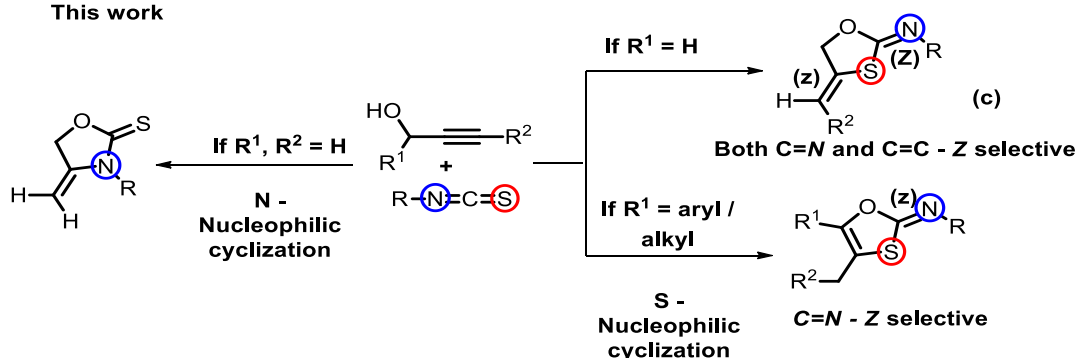
In 2014, D. H. Dethe et al



In 2017, M Nakka et al



This work



**Scheme 1** Use of isothiocyanate as potential ambient nucleophilic reagent in synthesis of novel heterocyclic framework

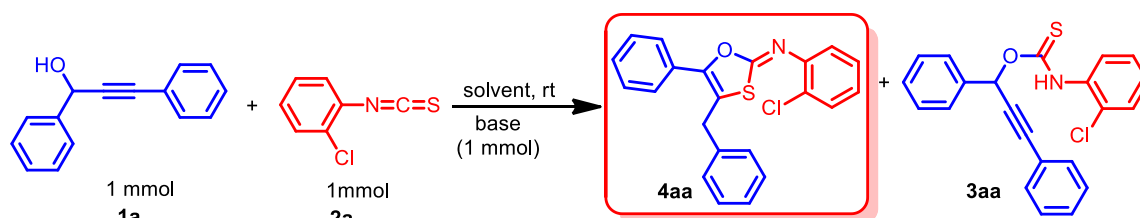
Being inspired by the wide ranging synthetic utility of isothiocyanate as versatile synthon, we envisioned to employ propargyl alcohol as a synthetic probe to study the isothiocyanate for atom specific cyclization. Notably, this study would disclose the stereochemical outcome around the C=X (X = C, N) bonds. Herein, we disclose the result on DBU assisted coupling and 5-*exo*-dig cyclization of isothiocyanate with internal 1° and 2° propargyl alcohol (Scheme 1c) to access 4-methylene oxazolidine-2-thiones, (*Z*)-*N*-(*Z*)-4-ethylidene-1,3-oxathiolan-2-ylidenes and (*Z*)-1,3-oxathiol-2-ylidenes respectively with high *Z*-selectivity. Further, isothiocyanate undergoes *N*-nucleophilic substitution with prop-2-yn-1-ol, a terminal alcohol to afford 4-methylene oxazolidine-2-thiones as exclusive product.

**RESULT AND DISCUSSION:** In order to find out the optimum reaction conditions, 1,3-diphenylprop-2-yn-1-ol (**1a**) and 1-chloro-2-isothiocyanatobenzene (**2a**) were chosen as substrate and reactant, respectively (Table 1). The first experiment was carried out in DCM as solvent with different organic bases at room temperature under nitrogen atmosphere. We could not isolate either heterocyclic

products nor insignificant amount of cyclized product, which was found to be N-(4-benzyl-5-phenyl-1,3-oxathiol-2-ylidene)-2-chloroaniline (**4aa**) (Table 1; entries 1-6). In most of the cases a noncyclized linear product was formed as the major component. In quest of the optimum condition, keeping the other factors unchanged, the reaction was further performed with DBU in acetonitrile as solvent and we were delighted to find that the cyclized product **4aa** (Table 1; entry 7) was afforded exclusively with excellent yield. Experiments with the inorganic carbonate bases ( $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$ ) and hydroxides (LiOH, NaOH and KOH) in DMF solvent mostly resulted with insignificant yield of **4aa** and significant yield of the uncyclized product (**3aa**) (Table 1; entries 8-13). When the reaction was carried out in sodium alkoxide bases like NaOMe, NaOEt and NaOtBu, **3aa** was formed as sole product (Table 1; entries 14-16); while the use of KOtBu and LiOtBu produced 32% and 45% of **4aa** (Table 1; entry 17-18), respectively. Here, the best yield for the synthesis of multisubstituted 1,3-oxathiol-2-ylidenes was accomplished with the condition mentioned in entry 7 of table 1 and thus considered as the optimum condition.

Having arrived at the optimum reaction conditions, the scope of the synthesis was examined with the broad range of isothiocyanates. The reactions with substituted 1,3-diphenylprop-2-yn-1-ol (Scheme 2) and the electron-deficient (-Cl<sup>14</sup>) or electron-rich (-OMe, -Me and -tBu<sup>15</sup>) substituted phenyl isothiocyanate delivered > 80% yield of **4aa-4ae**, irrespective of their position. Subsequently, 2-chloro phenyl isothiocyanate was screened with differently substituted 1,3-diphenylprop-2-yn-1-ol. 4-fluoro phenyl propargyl alcohol, explored on gram scale, produced an excellent yield of **4ba**. The other two different positional di-fluoro substituted propargyl alcohols and three-fluoro substituted propargyl alcohols were employed and identified as equally good substrates producing **4ca**, **4da** and **4ea** with 86%, 94% and 93% yield, respectively. Similarly, different halogen (Cl, F, Br) substituted phenyl propargyl alcohols were successfully coupled with 2-chloro phenyl isothiocyanate to afford excellent yields of **4ga-4ia**, and a propargyl alcohol with substituents R<sup>1</sup>= 4-*i*Pr produced 75% of **4ja**. In addition, propargyl alcohols carrying 4-Cl or 4-Br phenyl attached to C1 and 4-F phenyl attached to C3 were also productive when reacted with electron rich isothiocyanates, delivered moderate yields of **4mc**, **4hc** and **4hf**. The scope of the methodology was further tested using disubstituted pyridine propargyl alcohols produced the desired products **4ka** with good yields. In addition, the Boc protected indole substituted phenyl propargyl alcohol delivered the expected product **4la** with satisfactory yield.

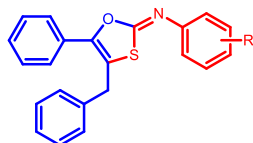
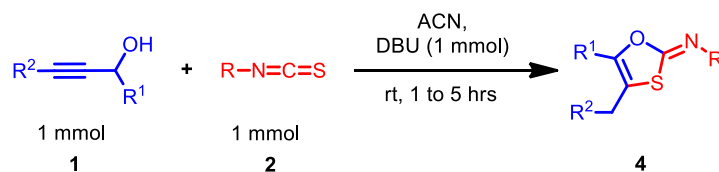
**Table 1: Study of optimum reaction conditions<sup>a</sup>**



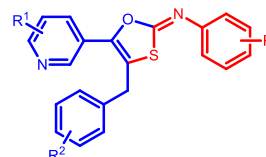
Entry	Solvent	Base	t (h)	% yield of 4aa	% yield of 3aa
1	DCM	DBU	72	15	50
2	DCM	DBN	72	18	50
3	DCM	DABCO	72	0	0
4	DCM	DIPEA	17	0	43
5	DCM	DBU	20	21	10
6	DCM	DBN	20	24	15
<b>7</b>	<b>ACN</b>	<b>DBU</b>	<b>1</b>	<b>88</b>	<b>0</b>
8	DMF	Na <sub>2</sub> CO <sub>3</sub>	15	0	0
9	DMF	K <sub>2</sub> CO <sub>3</sub>	15	0	32
10	DMF	Cs <sub>2</sub> CO <sub>3</sub>	15	0	53
11	DMF	LiOH	15	9	72
12	DMF	NaOH	15	16	60
13	DMF	KOH	15	0	63
14	DMF	NaOMe	15	0	68
15	DMF	NaOEt	15	0	82
16	DMF	NaOtBu	15	0	84
17	DMF	KOtBu	1	32	49
18	DMF	LiOtBu	1	45	42

[a]Yields of isolated products. DCM = dichloromethane, ACN = acetonitrile, DMF = N,N-dimethylformamide, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DBN = 1,5-diazabicyclo[4.3.0]non-5-ene, DABCO = 1,4-diazabicyclo[2.2.2]octane, DIPEA = di-isopropyl ethyl amine, Et = ethyl, *t*Bu = tertiary butyl, rt = room temperature, t = time, h = hour, N<sub>2</sub> = nitrogen.

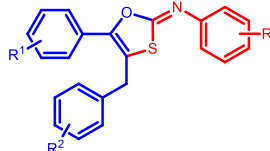
**Scheme 2: Scope of the synthesis of 3,4,5-trisubstituted (Z)-1,3-oxathiol-2-ylidenes<sup>a</sup>**



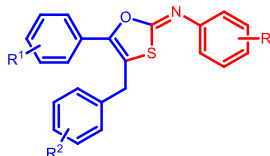
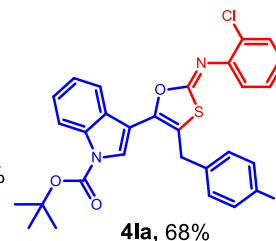
R = 2-Cl: **4aa**, 88%<sup>b</sup>  
 = 2-Me: **4ab**, 86%  
 = 4-*t*Bu: **4ac**, 89%<sup>b</sup>  
 = 2-OMe: **4ad**, 82%  
 = 3-OMe: **4ae**, 80%



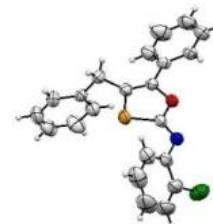
R = 2-Cl, R<sup>1</sup>: 5-Br, R<sup>2</sup>: H: **4ka**, 79%



R = 2-Cl, R<sup>1</sup>: H, R<sup>2</sup>: 4-F: **4ba**, 91%  
 R = 2-Cl, R<sup>1</sup>: 2-F, R<sup>2</sup>: 4-F: **4ca**, 86%  
 R = 2-Cl, R<sup>1</sup>: 2,5-F, R<sup>2</sup>: H: **4da**, 94%  
 R = 2-Cl, R<sup>1</sup>: 2,5-F, R<sup>2</sup>: 4-F: **4ea**, 93%  
 R = 2-Cl, R<sup>1</sup>: 4-Cl, R<sup>2</sup>: 4-F: **4fa**, 90%  
 R = 2-Cl, R<sup>1</sup>: 2-Cl-5-NO<sub>2</sub>, R<sup>2</sup>: H: **4ga**, 92%  
 R = 2-Cl, R<sup>1</sup>: 4-Br, R<sup>2</sup>: 4-F: **4ha**, 89%  
 R = 2-Cl, R<sup>1</sup>: 4-Br, R<sup>2</sup>: H: **4ia**, 77%  
 R = 2-Cl, R<sup>1</sup>: 4-*i*Pr, R<sup>2</sup>: H: **4ja**, 75%



R = 4-*t*Bu, R<sup>1</sup>: 4-Cl, R<sup>2</sup>: H: **4mc**, 73%  
 R = 4-*t*Bu, R<sup>1</sup>: 4-Br, R<sup>2</sup>: 4-F: **4hc**, 78%  
 R = 4-OCH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>, R<sup>1</sup>: 4-Br, R<sup>2</sup>: 4-F: **4hf**, 83%

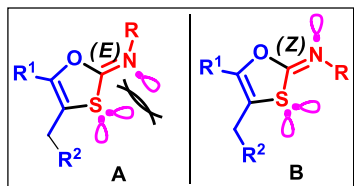


**4aa**

[a] Reaction conditions: **1** (4.80 mmol), **2** (4.80 mmol), DBU (4.80 mmol) in 10 volume of ACN wrt **1** under N<sub>2</sub> atmosphere. [b] Reactions were carried out on gram scale

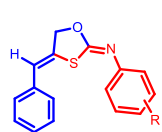
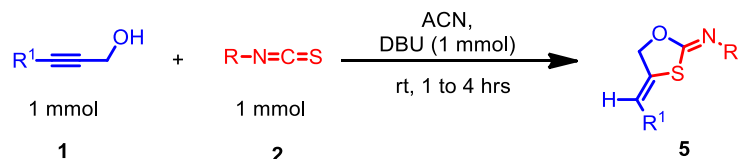
It is worth mentioning that our newly synthesized 1,3-oxathiol-2-ylidene compounds with chloro and bromo substituents could be considered as potential candidates for different transition metal catalyzed coupling reaction including Suzuki<sup>15</sup> and Sonogashira<sup>16</sup> to generate more complex molecular architecture. Most importantly, out of all the reactions enlisted in Scheme 2, isothiocyanates reacted exclusively with S-nucleophilic sites resulting in the formation of 1,3-oxathiol-2-ylidene as sole product. At this point, what remained unknown is the stereochemical outcome around C=N bond. In order to confirm the selectivity in imine, X-ray structure determination was carried out on the compound **4aa**<sup>14</sup> which gave good crystal and the structure determination disclosed the stereochemistry around C=N bond is *Z*. This unprecedented

selection of *Z* isomer of imine is somewhat rare. As shown in figure 1, *E*-isomer would face severe electron-electron repulsion between the lone pairs in 2p-lobes of nitrogen and relatively large 3p-lobes of sulfur and thus highly disfavored whereas, the *Z*-isomer has minimal electron-electron repulsions between the lone pairs in 2p-lobes of nitrogen and 2p-lobes of oxygen which results in the exclusive *Z*-selectivity. Also, this observation is in line with Gálvez<sup>17</sup> et al previous report where they described that the *Z*-isomer is indeed more stable than *E*-isomer.

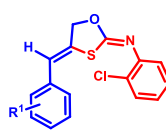


**Figure 1:** Selectivity in imine

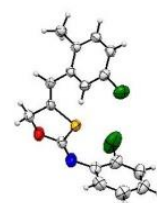
**Scheme 3:** Scope of the synthesis of 3,4-disubstituted (*Z*)-*N*-(*Z*)-4-ethylidene-1,3-oxathiolan-2-ylidenes<sup>a</sup>



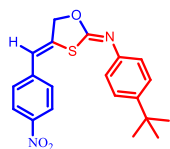
R = 2-Cl: **5a**, 88%  
 = 2-Me: **5nb**, 82%  
 = 2-OMe: **5nd**, 71%<sup>b</sup>  
 = 3-OMe: **5ne**, 73%<sup>b</sup>  
 = 4-*t*Bu: **5nc**, 86%



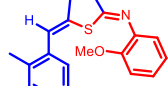
R<sup>1</sup> = 4-NO<sub>2</sub>: **5oa**, 90%  
 = 2,3-F: **5pa**, 87%  
 = 2-OMe-5-Cl: **5qa**, 77%  
 = 2-Me-5-Cl: **5ra**, 83%  
 = 4-Me: **5sa**, 88%



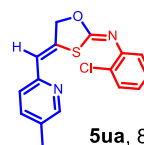
**5a**



**5oc**, 92%



**5td**, 89%

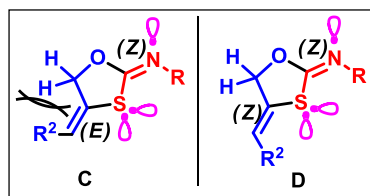


**5ua**, 81%

[a] Reaction conditions: **1** (4.80 mmol), **2** (4.8058 mmol), DBU (4.80 mmol) in 10 volume of ACN wrt **1** under N<sub>2</sub> atmosphere. [b] Reaction was carried out on gram scale.

Prompted by the successful synthesis of multisubstituted (*Z*)-1,3-oxathiol-2-ylidenes from secondary propargyl alcohols, the same synthetic procedure was employed with primary propargyl alcohols. This time *N*-4-ethylidene-1,3-oxathiolan-2-ylidenes was found to be the sole product as depicted in Scheme 3. Firstly, 3-phenyl-prop-2-yn-1-ol was tested separately with six different aromatic isothiocyanates; for

example the *ortho* substituted (2-Cl or 2-Me) isothiocyanates yielded 88% of **5na** and 82% of **5nb**. The gram scale synthesis from electron rich methoxy substituents attached to *ortho* or *meta* positions of aromatic isothiocyanates were well transformed to the desired products of **5nd** and **5ne** with satisfactory yields. Similarly *p*-*t*Bu and *p*-Br substituted phenyl at C-3 of propargyl alcohols underwent smooth reaction, affording good to excellent yields of **5nc** and **5ng**, respectively. This reaction was further applied to six different substituted phenyl prop-2-yn-1-ols with two isothiocyanates. The 4-nitro and di-fluoro substituted aromatic propargyl alcohols undergone coupling and cyclization smoothly with 2-chloro phenyl isothiocyanate and afforded 90% of **5oa** and 87% of **5pa**. The disubstituted, substituents being -Cl and -OMe or -Cl and -Me, propargyl alcohols were producing very good yields of **5qa** and **5ra**; the 3-(*p*-tolyl)prop-2-yn-1-ol, 3-(5-chloro-2-methylphenyl)prop-2-yn-1-ol and 3-(5-methyl-pyridin-2-yl) Prop-2-yn-1-ol were equally effective, forming 88% of **5sa**, 89% of **5td** and 81% of **5ua**. The 3-(4-nitrophenyl)prop-2-yn-1-ol reacting with 1-(tert-butyl)-4-isothiocyanatobenzene gave 92% of **5oc**. Thus, the reaction was found to be highly successful even with primary propargyl alcohol. Again we were curious to know the selectivity around the C=N bond. The careful analysis of NMR spectra once again, revealed that the reaction is stereoselective since we are isolating only single isomer. X-ray crystal analysis of **5ra**<sup>18</sup> revealed that the stereochemical outcome in alkene is *Z* as well. This can be explained as shown in figure 2 where *E*-isomer is highly disfavoured due to severe A<sup>1,3</sup>-strain<sup>19</sup> between the hydrogen and aryl group. Such strain is not present in the *Z*-isomer. This attributes to the exclusive *Z*-selectivity in the alkene. Further, as anticipated, the imine remained *Z*-selective. Thus we have synthesized N-4-ethylidene-1,3-oxathiolan-2-ylidenes with high dual *Z*-selectivity.



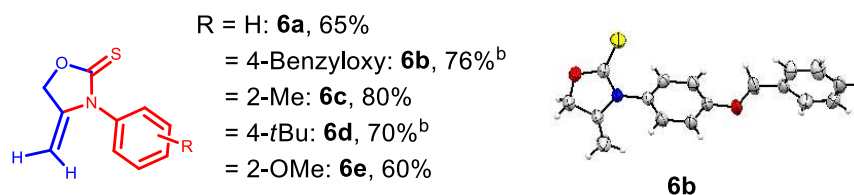
**Figure 2:** Selectivity in alkene

Finally, prop-2-yn-1-ol was treated with phenyl isothiocyanates under optimized reaction condition and the product was found to be oxazolidine-2-thiones derivative **6a** with good yield (Scheme 4). Unlike the reactions of isothiocyanate with secondary and primary propargyl alcohols, the nucleophilic attack took



place via N-atom to afford oxazolidine-2-thione. Subsequently, we carried out the reaction with differently substituted phenyl isothiocyanates (4-OBn, 2-Me, 4-tBu and 2-OMe) and delivered isolated products of oxazolidine-2-thiones derivatives **6b-6e** with moderate to excellent yield. Once again, we were fortunate to have a suitable crystal of compound **6b**<sup>20</sup> for crystallographic study which confirm the structural assignment unambiguously.

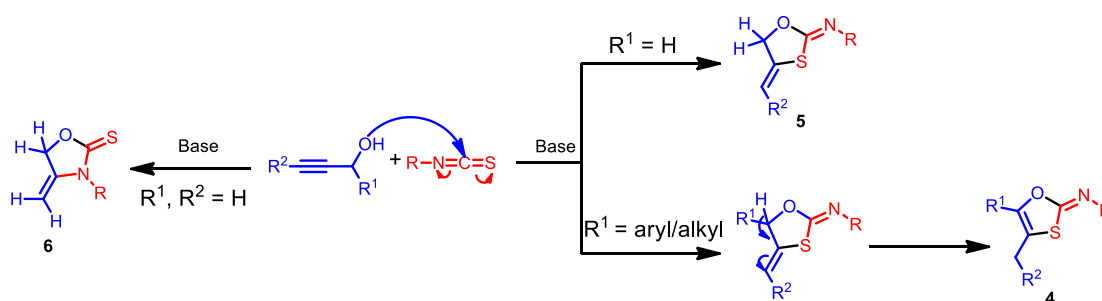
#### Scheme 4: Scope of the synthesis of 3-substituted 4-methylene-oxazolidine-2-thiones<sup>a</sup>



[a] Reaction conditions: **1** (4.80 mmol), **2** (4.8058 mmol), DBU (4.80 mmol) in 10 volume of ACN wrt **1** under N<sub>2</sub> atmosphere. [b] Reaction was carried out on gram scale.

The possible reaction mechanism has been proposed in Scheme 5. DBU de-protonates the hydroxyl group in terminal primary propargyl alcohol and subsequently the corresponding N-anion in Isothiocyanates attacks the alkyne through a 5-*exo*-dig mode to get oxazolidine-2-thiones (**6**). In internal primary propargyl alcohol, 5-*exo*-dig cyclization of S-anion in isothiocyanate attacks the alkyne to get **5**. In case of internal secondary propargyl alcohol, the S-anion led to the formation of exocyclic olefin which quickly rearranges through 1,3-hydrogen shift to form more substituted endocyclic olefin **4**.

#### Scheme 5: Plausible reaction mechanism



## CONCLUSION

A new synthetic protocol have been demonstrated for synthesizing 3,4,5-substituted (*Z*)-1,3-oxathiol-2-ylidenes, 3,4-disubstituted (*Z*)-N-(*Z*)-4-ethylidene-1,3-oxathiolan-2-ylidenes and 4-methylene-oxazolidine-2-thiones by reacting isothiocyanates with internal secondary, primary and terminal primary propargyl alcohols, respectively. Interestingly, the site of nucleophilic attack of isothiocyanate was found to be different, either S-nucleophilic or N-nucleophilic was achieved depends on the nature of propargyl alcohol. Moreover, the stereochemical arrangement of various groups around C=N and C=C were found to be quite significant. The high *Z*-selectivity in imine is favored because there is no repulsion between the lone pairs in sulfur and nitrogen as they are placed far away around C=N bond. In case of alkene selectivity, the lack of 1,3-allylic steric strain between hydrogen and aryl group plays an important role in favoring *Z*-alkene. It is worth mentioning that the cyclization is highly atom specific and leading to stereoselectivity around C=N and C=C bond which is rare and unique outcome of this study.

## EXPERIMENTAL SECTION

**General.**  $^1\text{H}$  and  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectra were recorded at 300/ 400 (75/100) MHz spectrometers, respectively and the spectral data were reported in ppm relative to tetramethylsilane (TMS) as the internal standard. Mass spectra were recorded by electron ionization. IR spectra were recorded on an FT-IR spectrometer, and major peaks were reported in  $\text{cm}^{-1}$ . TLC was performed by using commercially available 100-400 mesh silica gel plates (GF254). Unless and otherwise mentioned, the purchased chemicals were used without further purification.

**General procedure for the synthesis of secondary propargyl alcohols (1a-1m).** To an oven dried multi-necked round bottom flask (RBF) were added corresponding phenyl acetylene (0.100mol) and tetrahydrofuran (THF), sequentially under nitrogen atmosphere. The reaction mixture was cooled to  $-70^\circ\text{C}$ . 2.0M solution of *n*-BuLi in hexane (0.090mol) at  $-70^\circ\text{C}$  was added and the reaction mixture was

stirred at the same temperature for about 20 minutes. Then a solution of corresponding benzaldehyde (0.067mol) in tetrahydrofuran at -70 °C was added to the reaction mixture which was stirred at the same temperature for about 10 minutes. The progress of the reaction was monitored by thin layer chromatogram (TLC) and at the completion of the reaction the reaction mixture was quenched with aqueous NH<sub>4</sub>Cl solution and then extracted with ethyl acetate. The organic layer washed with aqueous NH<sub>4</sub>Cl solution, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated at reduced pressure to give a light brown liquid. The crude sample was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to give the desired secondary propargyl alcohols.

**General procedure for the synthesis of primary propargyl alcohols (1n-1u).** To an oven dried multi-necked RBF were added corresponding iodobenzene (0.057mol), prop-2-yn-1-ol (0.085mol), acetonitrile (ACN), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (2.844mmol), CuI (2.844 mmol) and triethyl amine (0.142mol) were successively added under nitrogen atmosphere at room temperature. The reaction mixture was heated to 80 °C and stirred at the same temperature for 2 h. Completion of the reaction was asserted by TLC and then the reaction mixture was quenched with aqueous ammonia solution. The reaction mixture was extracted with ethyl acetate, and the organic layer washed with brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated at reduced pressure to give a dark brown liquid. The crude sample was purified by chromatography on silica gel (petroleum ether/ ethyl acetate = 1/1) to give the desired primary propargyl alcohols.

**General procedure for the synthesis of 3,4,5-trisubstituted (Z)-1,3-oxathiol-2-ylidenes.**

**(Z)-N-(4-benzyl-5-phenyl-1,3-oxathiol-2-ylidene)-2-chloroaniline (4aa):** To a solution of **1a** (120 mg, 0.576 mmol) in ACN (1.2 mL) was added successively 1-chloro-2-isothiocyanato-benzene (**2a**) (97.4 mg, 0.576 mmol) and DBU (87.7 mg, 0.576 mmol) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for about 1 hr and then quenched into ice-water (25 mL), extracted with MTBE (25 mL), and the organic layer washed with brine solution (25 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Then the filtrate was stirred along with silica gel (500 mg) for 0.5 hr, filtered and concentrated at a reduced pressure to get 191 mg of **4aa**, 88% yield; yellow amorphous solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 6 Hz, 2H), 7.45-7.21 (m, 7H), 7.20-7.04 (m, 5H), 3.98 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 163.6, 146.2, 144.3, 137.4, 130.8, 129.9, 129.4, 129.2, 128.7, 128.5, 128.3, 128.0, 127.8, 127.3,

125.9, 122.1, 114.2, 33.2; IR (KBr)  $\nu_{\max}$ : 2929.9, 2155.4, 1765.8, 1657.4, 1485.9, 1333.3, 1086.7, 853.2, 759.1, 705.3  $\text{cm}^{-1}$ ; MS (ESI): 378.30 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>22</sub>H<sub>16</sub>CINOS: C, 69.92; H, 4.27; N, 3.71. Found: C, 69.85; H, 4.18; N, 3.76.

**(Z)-N-(4-benzyl-5-phenyl-1,3-oxathiol-2-ylidene)-2-methylaniline (4ab):** 95 mg, 86% yield; yellow gummy solid; <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65-7.61 (m, 2H), 7.43 (dd, *J* = 5.6, 6.4 Hz, 3H), 7.33-7.25 (m, 3H), 7.22-7.13 (m, 4H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 3.96 (s, 2H), 2.24 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.4, 148.1, 144.0, 137.6, 131.4, 130.7, 129.9, 129.4, 129.3, 128.7, 128.0, 127.8, 127.5, 125.0, 120.2, 114.0, 33.3, 18.3; IR (KBr)  $\nu_{\max}$ : 2909.9, 2125.4, 1755.8, 1657.9, 1482.9, 1334.3, 1066.7, 843.2, 779.1, 709.3  $\text{cm}^{-1}$ ; MS (ESI): 358.20 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>23</sub>H<sub>19</sub>NOS: C, 77.28; H, 5.36; N, 3.92. Found: C, 77.32; H, 5.25; N, 3.87.

**(Z)-N-(4-benzyl-5-phenyl-1,3-oxathiol-2-ylidene)-4-(tert-butyl)aniline (4ac):** 104 mg, 89% yield; yellow solid; <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69-7.67 (m, 2H), 7.40-7.34 (m, 5H), 7.19-7.15 (m, 3H), 6.99 (d, *J* = 4.8 Hz, 2H), 6.85 (d, *J* = 2.8 Hz, 2H), 3.90 (s, 2H), 1.32 (s, 9H); <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  163.6, 152.9, 144.2, 135.3, 131.9, 129.0, 128.7, 127.8, 127.3, 127.0, 126.8, 126.5, 125.5, 125.4, 34.8, 31.2, 29.7; IR (KBr)  $\nu_{\max}$ : 2729.9, 2159.4, 1785.8, 1677.2, 1425.0, 1313.3, 1286.7, 833.2, 750.1, 715.0  $\text{cm}^{-1}$ ; MS (ESI): 400.30 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>26</sub>H<sub>25</sub>NOS: C, 78.16; H, 6.31; N, 3.51. Found: C, 78.23; H, 6.27; N, 3.46.

**(Z)-N-(4-benzyl-5-phenyl-1,3-oxathiol-2-ylidene)-2-methoxyaniline (4ad):** 76 mg, 82% yield; yellow solid; <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70-7.67 (m, 2H), 7.45-7.35 (m, 4H), 7.16 (dd, *J* = 4 Hz, 3H), 7.00-6.92 (m, 1H), 6.90-6.87 (m, 4H), 3.95-3.76 (m, 2H), 3.60 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.2, 154.9, 144.0, 135.3, 131.5, 129.8, 129.0, 128.8, 128.5, 127.9, 127.0, 126.9, 125.9, 125.3, 123.0, 120.9, 112.3, 55.6, 29.7; IR (KBr)  $\nu_{\max}$ : 3020.7, 2023.7, 1950.7, 1599.9, 1498.3, 1396.1, 1328.7, 1426.2, 1210.1, 1067.2, 818.2, 759.1  $\text{cm}^{-1}$ ; MS (ESI): 374.00 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub>S: C, 73.97; H, 5.13; N, 3.75. Found: C, 73.90; H, 5.10; N, 3.66.

**(Z)-N-(4-benzyl-5-phenyl-1,3-oxathiol-2-ylidene)-3-methoxyaniline (4ae):** 54 mg, 80% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63-7.61 (m, 2H), 7.43 (d,  $J = 7.2$  Hz, 3H), 7.32 (dd,  $J = 4.4, 7.2$  Hz, 3H), 7.28-7.21 (m, 3H), 6.67-6.60 (m, 3H), 4.00 (s, 2H), 3.79 (s, 3H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.1, 150.3, 143.9, 137.6, 130.8, 129.8, 129.4, 129.2, 128.9, 128.7, 127.9, 127.7, 126.4, 113.8, 113.5, 110.8, 107.3, 55.7, 33.2; IR (KBr)  $\nu_{\text{max}}$ : 2979.9, 2095.4, 1725.8, 1667.9, 1455.9, 1293.3, 1096.7, 850.2, 749.1, 709.0  $\text{cm}^{-1}$ ; MS (ESI): 374.00 ( $\text{M}+\text{H}$ ) $^+$ ; Anal. Calcd for  $\text{C}_{23}\text{H}_{19}\text{NO}_2\text{S}$ : C, 73.97; H, 5.13; N, 3.75. Found: C, 73.90; H, 5.10; N, 3.65.

**(Z)-2-chloro-N-(4-(4-fluorobenzyl)-5-phenyl-1,3-oxathiol-2-ylidene)aniline (4ba):** 178.2 mg, 91% yield; yellow solid.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66-7.45 (m, 2H), 7.44-7.40 (m, 4H), 7.26-7.16 (m, 3H), 7.07-6.98 (m, 4H), 3.95 (s, 2H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (244.6Hz), 146.2, 144.3, 133.2, 130.8, 130.3, 130.2, 130.0, 129.3, 128.4, 128.0, 127.2, 126.0, 122.1, 116.4, 116.2, 114.1, 32.5; IR (KBr)  $\nu_{\text{max}}$ : 2979.1, 2091.4, 1745.6, 1637.9, 1455.9, 1263.3, 1066.2, 850.2, 779.1, 719.0  $\text{cm}^{-1}$ ; MS (ESI): 396.30 ( $\text{M}+\text{H}$ ) $^+$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{15}\text{ClFNOS}$ : C, 66.75; H, 3.82; N, 3.54. Found: C, 66.83; H, 3.80; N, 3.51.

**(Z)-2-chloro-N-(4-(4-fluorobenzyl)-5-(2-fluorophenyl)-1,3-oxathiol-2-ylidene)aniline (4ca):** 83 mg, 86% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.41 (m, 2H), 7.28-6.95 (m, 10H), 3.74 (s, 2H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 158.7, 146.0, 138.2, 133.0 (3 Hz), 132.4 (8.2 Hz), 131.5, 130.8, 130.5 (8 Hz), 130.2 (8.2 Hz), 128.4, 127.2, 126.0, 125.0, 122, 117.7, 116.8 (21.7 Hz), 116.4 (14.1 Hz), 116.1 (22 Hz), 32.5; IR (KBr)  $\nu_{\text{max}}$ : 2939.5, 2045.4, 1705.8, 1647.9.5, 1405.9, 1253.3, 1056.7, 859.2, 789.1, 721.0  $\text{cm}^{-1}$ ; MS (ESI): 414.20 ( $\text{M}+\text{H}$ ) $^+$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{14}\text{ClF}_2\text{NOS}$ : C, 63.85; H, 3.41; N, 3.38. Found: C, 63.79; H, 3.37; N, 3.31.

**(Z)-N-(4-benzyl-5-(2,5-difluorophenyl)-1,3-oxathiol-2-ylidene)-2-chloroaniline (4da):** 116 mg, 94% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (dd,  $J = 1.2$  Hz, 1H), 7.31-7.25 (m, 3H), 7.23-7.15 (m, 6H), 7.04 (t,  $J = 7.2$  Hz, 2H), 3.78 (s, 2H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5 (288Hz), 155.9 (308Hz), 145.9, 137.1, 136.9, 130.8, 129.3, 128.9, 128.4, 127.9, 127.2, 126.0, 121.9, 119.1 (9Hz), 119.0, 118.8 (8.6Hz), 118.2 (8.6Hz), 118.0 (8.6Hz), 117.1 (24.8Hz), 33.3 (4.6Hz); IR (KBr)  $\nu_{\text{max}}$ : 2979.2, 2015.4,

1705.0, 1677.9.5, 1405.0, 1253.9, 1066.7, 859.0, 759.1, 711.0  $\text{cm}^{-1}$ ; MS (ESI): 414.20 (M+H)<sup>+</sup>; Anal. Calcd for  $\text{C}_{22}\text{H}_{14}\text{ClF}_2\text{NOS}$ : C, 63.85; H, 3.41; N, 3.38. Found: C, 63.82; H, 3.37; N, 3.30.

**(Z)-2-chloro-N-(5-(2,5-difluorophenyl)-4-(4-fluorobenzyl)-1,3-oxathiol-2-ylidene)aniline (4ea):** 120 mg, 93% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45-7.30 (m, 2H), 7.25-7.14 (m, 5H), 7.09-6.98 (m, 4H), 3.77 (s, 2H);  $^{13}\text{C}$  {1H} NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 160.9, 159.7, 136.5, 132.3, 130.4, 130.1, 130.0, 127.9, 126.7, 125.6, 121.4, 118.7, 117.8, 117.7, 117.6, 117.5, 117.2, 115.9, 115.7, 32.1; IR (KBr)  $\nu_{\text{max}}$ : 2929.9, 2109.4, 1755.8, 1670.4, 1405.0, 1313.0, 1286.7, 853.2, 750.1, 705.0  $\text{cm}^{-1}$ ; MS (ESI): 432.04 (M+H)<sup>+</sup>; Anal. Calcd for  $\text{C}_{22}\text{H}_{13}\text{ClF}_3\text{NOS}$ : C, 61.19; H, 3.03; N, 3.24. Found: C, 62.01; H, 3.20; N, 3.22.

**(Z)-2-chloro-N-(5-(4-chlorophenyl)-4-(4-fluorobenzyl)-1,3-oxathiol-2-ylidene)aniline (4fa):** 97 mg, 90% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.53 (m, 2H), 7.46-7.32 (m, 3H), 7.27-7.15 (m, 3H), 7.05-6.99 (m, 4H), 3.92 (s, 2H);  $^{13}\text{C}$  {1H} NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (244.7 Hz), 144.6 (282.8 Hz), 136.0, 132.8, 130.8, 130.2, 130.1, 129.6, 129.1, 128.4, 127.2, 126.8, 126.0, 122.0, 116.5, 116.3, 114.8, 32.5; IR (KBr)  $\nu_{\text{max}}$ : 2909.9, 2045.4, 1725.1, 1667.9, 1395.1, 1293.3, 1090.6, 850.7, 759.1, 709.5  $\text{cm}^{-1}$ ; MS (ESI): 430.50 (M+H)<sup>+</sup>; Anal. Calcd for  $\text{C}_{22}\text{H}_{14}\text{Cl}_2\text{FNOS}$ : C, 61.40; H, 3.28; N, 3.25. Found: C, 61.33; H, 3.22; N, 3.22.

**(Z)-N-(4-benzyl-5-(2-chloro-5-nitrophenyl)-1,3-oxathiol-2-ylidene)-2-chloroaniline (4ga):** 78 mg, 92% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (s, 1H), 8.27 (s, 1H), 7.70 (d,  $J = 8.8$  Hz, 1H), 7.42 (d,  $J = 3.2$  Hz, 1H), 7.31-7.20 (m, 4H), 7.13-7.00 (m, 4H), 3.70 (s, 2H);  $^{13}\text{C}$  {1H} NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 146.8, 145.7, 142.2, 136.4, 131.8, 130.9, 129.7, 129.4, 128.8 (2), 128.4, 128.2, 128.0, 127.8, 126.5, 126.2, 121.9, 33.3; IR (KBr)  $\nu_{\text{max}}$ : 2947.0, 2091.4, 1720.8, 1667.9, 1455.9, 1293.3, 1096.2, 850.2, 749.1, 04.0  $\text{cm}^{-1}$ ; MS (ESI): 457.00 (M+H)<sup>+</sup>; Anal. Calcd for  $\text{C}_{22}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_3\text{S}$ : C, 57.78; H, 3.09; N, 6.13. Found: C, 57.83; H, 3.12; N, 6.19.

**(Z)-N-(5-(4-bromophenyl)-4-(4-fluorobenzyl)-1,3-oxathiol-2-ylidene)-2-chloroaniline (4ha):** 103 mg, 89% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59-7.40 (m, 4H), 7.23-7.14 (m, 4H), 7.07-6.98 (m, 4H),

3.92 (s, 2H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 160.9, 142.7, 132.4, 130.4, 129.7, 129.3, 128.9, 127.9, 126.9, 126.7, 125.6, 123.8, 121.5, 116.0, 115.8, 115.6, 32.1; IR (KBr)  $\nu_{\text{max}}$ : 2929.1, 2095.4, 1725.8, 1667.9, 1459.9, 1293.9, 1066.7, 850.2, 749.6, 719.0  $\text{cm}^{-1}$ ; MS (ESI): 474.10 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{14}\text{BrClFNOS}$ : C, 55.66; H, 2.97; N, 2.95. Found: C, 55.74; H, 2.91; N, 2.85.

**(Z)-N-(4-benzyl-5-(4-bromophenyl)-1,3-oxathiol-2-ylidene)-2-chloroaniline (4ia)**: 83 mg, 77% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.45 (m, 4H), 7.43-7.28 (m, 4H), 7.22-7.22 (m, 3H), 7.09-7.05 (m, 2H), 3.97 (s, 2H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5, 145.7, 142.7, 136.7, 132.0, 131.9, 131.8, 130.4, 130.0, 129.6, 129.4, 129.0, 128.9, 128.5, 128.2, 127.9, 127.6, 127.5, 126.9, 126.8, 126.5, 125.5, 123.7, 121.6, 115.9, 114.6, 32.8; IR (KBr)  $\nu_{\text{max}}$ : 2999.9, 2095.4, 1725.8, 1467.2, 1455.9, 1303.3, 1076.7, 850.2, 749.8, 700.0  $\text{cm}^{-1}$ ; MS (ESI): 456.97 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{22}\text{H}_{15}\text{BrClNOS}$ : C, 57.85; H, 3.31; N, 3.07. Found: C, 57.99; H, 3.42; N, 3.14.

**(Z)-N-(4-benzyl-5-(4-isopropylphenyl)-1,3-oxathiol-2-ylidene)-2-chloroaniline (4ja)**: 68 mg, 75% yield; semi yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61-7.59 (m, 2H), 7.45-7.22 (m, 9H), 7.10-7.05 (m, 1H), 4.01 (s, 2H), 3.02-2.95 (m, 1H), 1.32-1.30(d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 150.4, 145.9, 144.0, 137.1, 130.3, 128.9, 128.2, 127.8, 127.5, 127.2, 126.8, 125.5, 125.3, 121.7, 112.8, 34.0, 32.7, 23.7; IR (KBr)  $\nu_{\text{max}}$ : 2999.2, 2015.0, 1645.0, 1677.9.5, 1405.0, 1233.9, 1066.7, 859.0, 759.1, 703.0  $\text{cm}^{-1}$ ; MS (ESI): 420.11 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{25}\text{H}_{22}\text{ClNOS}$ : C, 71.50; H, 5.28; N, 3.34. Found: C, 71.68; H, 5.38; N, 3.51.

**(Z)-N-(4-benzyl-5-(4-chlorophenyl)-1,3-oxathiol-2-ylidene)-4-(tert-butyl)aniline (4mc)**: 76 mg, 73% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 8.8$  Hz, 2H), 7.42 (d,  $J = 8.4$  Hz, 2H), 7.36-7.27 (m, 5H), 7.21 (d,  $J = 6.8$  Hz, 2H), 6.98 (d,  $J = 8.8$  Hz, 2H), 3.95 (s, 2H), 1.30 (s, 9H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 140.1, 138.5, 137.2, 136.9, 135.3, 129.0, 128.9, 128.7, 128.1, 127.4, 126.4, 120.5, 113.8, 34.4, 32.8, 31.4; IR (KBr)  $\nu_{\text{max}}$ : 2079.2, 2015.4, 1705.0, 1779.5, 1405.0, 1293.3, 1066.7, 859.0, 759.1, 701.0  $\text{cm}^{-1}$ ; MS (ESI): 434.10 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{26}\text{H}_{24}\text{ClNOS}$ : C, 71.95; H, 5.57; N, 3.23. Found: C, 71.97; H, 5.51; N, 3.34.

**(Z)-N-(5-(4-bromophenyl)-4-(4-fluorobenzyl)-1,3-oxathiol-2-ylidene)-4-(tert-butyl)aniline (4hc):** 82 mg, 78% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 8.4$  Hz, 2H), 7.47 (d,  $J = 8.8$  Hz, 2H), 7.34 (d,  $J = 8.8$  Hz, 2H), 7.17 (d,  $J = 8.4$  Hz, 2H), 7.00 (dd,  $J = 8.4$  Hz, 4H), 3.91 (s, 2H), 1.30 (s, 9H);  $^{13}\text{C}$  {1H} NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 145.4, 133.0, 132.9, 132.5, 130.2, 130.1, 129.3, 127.5, 126.9, 124.1, 120.9, 116.5, 116.2, 114.2, 34.9, 32.5, 31.8; IR (KBr)  $\nu_{\text{max}}$ : 3079.2, 2015.4, 1745.0, 1679.5, 1385.0, 1253.2, 1066.7, 859.0, 709.1, 711.0  $\text{cm}^{-1}$ ; MS (ESI): 496.10 ( $\text{M}+\text{H}$ ) $^+$ ; Anal. Calcd for  $\text{C}_{26}\text{H}_{23}\text{BrFNOS}$ : C, 62.90; H, 4.67; N, 2.82. Found: C, 62.97; H, 4.71; N, 2.76.

**(Z)-4-(benzyloxy)-N-(5-(4-bromophenyl)-4-(4-fluorobenzyl)-1,3-oxathiol-2-ylidene)aniline (4hf):** 96 mg, 83% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.59 (m, 2H), 7.58-7.49 (m, 2H), 7.48-7.45 (m, 3H), 7.43-7.39 (m, 3H), 7.19-6.96 (m, 2H), 6.88-6.82 (m, 4H), 5.05 (d,  $J = 14.4$  Hz, 2H), 3.90 (d,  $J = 26$  Hz, 2H);  $^{13}\text{C}$  {1H} NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 142.8, 137.4, 136.6, 132.7, 131.0, 130.2, 129.7, 129.3, 128.7, 128.4, 128.0, 127.9, 127.3, 126.2, 124.1, 123.1, 116.3, 114.2, 32.5, 29.5; IR (KBr)  $\nu_{\text{max}}$ : 2959.2, 2015.4, 1755.0, 1677.3, 1385.0, 1253.9, 1066.7, 889.0, 759.1, 701.5  $\text{cm}^{-1}$ ; MS (ESI): 546.20 ( $\text{M}+\text{H}$ ) $^+$ ; Anal. Calcd for  $\text{C}_{29}\text{H}_{21}\text{BrFNO}_2\text{S}$ : C, 63.74; H, 3.87; N, 2.56. Found: C, 63.64; H, 3.75; N, 2.50.

**(Z)-N-(4-benzyl-5-(5-bromopyridin-3-yl)-1,3-oxathiol-2-ylidene)-2-chloroaniline (4ka):** 75 mg, 79% yield; semi yellow solid;  $^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (s, 1H), 8.70 (s, 1H), 8.17 (s, 1H), 7.40 (d,  $J = 7.8$  Hz, 1H), 7.34-7.32 (m, 3H), 7.26-7.20 (m, 3H), 7.09-7.02 (m, 2H), 3.99 (s, 2H);  $^{13}\text{C}$  {1H} NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0, 150.7, 145.7, 145.4, 139.2, 138.2, 136.2, 130.9, 129.6, 128.6, 128.4, 128.2, 127.1, 126.3, 121.8, 118.9, 33.2; IR (KBr)  $\nu_{\text{max}}$ : 3029.9, 2009.4, 1755.2, 1670.4, 1445.0, 1313.0, 1286.5, 853.2, 750.1, 709.0  $\text{cm}^{-1}$ ; MS (ESI): 457.20 ( $\text{M}+\text{H}$ ) $^+$ ; Anal. Calcd for  $\text{C}_{21}\text{H}_{14}\text{BrClN}_2\text{OS}$ : C, 55.10; H, 3.08; N, 6.12. Found: C, 55.18; H, 3.14; N, 6.17.

**(Z)-tert-butyl 3-(2-((2-chlorophenyl)imino)-4-(4-fluorobenzyl)-1,3-oxathiol-5-yl)-1H-indole-1-carboxylate (4la):** 65 mg, 68% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J = 7.2$  Hz, 1H), 7.92 (d,  $J = 6.4$  Hz, 1H), 7.80 (s, 1H), 7.52-7.30 (m, 3H), 7.26-7.17 (m, 3H), 7.07 (d,  $J = 7.6$  Hz, 2H), 7.00 (d,  $J$



= 8.4 Hz, 2H), 3.92 (s, 2H), 1.53 (s, 9H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 144.1, 143.1, 137.9, 137.0, 136.0, 135.5, 134.0, 130.9, 130.2, 128.4, 126.1, 124.0, 122.3, 121.8, 116.4, 116.2, 115.7, 59.7, 32.0, 28.6; IR (KBr)  $\nu_{\text{max}}$ : 2979.2, 2015.4, 1705.0, 1677.9, 1405.0, 1253.9, 1066.7, 859.0, 759.1, 717.0  $\text{cm}^{-1}$ ; MS (ESI): 535.20 ( $\text{M}+\text{H}$ ) $^+$ ; Anal. Calcd for  $\text{C}_{29}\text{H}_{24}\text{ClFN}_2\text{O}_3\text{S}$ : C, 65.10; H, 4.52; N, 5.24. Found: C, 65.19; H, 4.58; N, 5.34.

**General procedure for synthesis of 3,4-disubstituted (Z)-N-(Z)-4-ethylidene-1,3-oxathiolan-2-ylidenes.**

**(Z)-N-((Z)-4-benzylidene-1,3-oxathiolan-2-ylidene)-2-chloroaniline (5na):** To a solution of **1n** (125 mg, 0.946 mmol) in ACN (1.2 mL) was added successively 1-chloro-2-isothiocyanato-benzene (**2a**) (160 mg, 0.946 mmol) and DBU (144 mg, 0.946 mmol) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for about 1 hr and then quenched into ice-water (25 mL), extracted with MTBE (25 mL), and the organic layer washed with brine solution (25 mL), dried over  $\text{Na}_2\text{SO}_4$  and filtered. Then the filtrate was stirred along with silica gel (500 mg) for 0.5 hr, filtered and concentrated at a reduced pressure to obtain 250.7 mg, 88% yield; pale yellow solid.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.38 (m, 2H), 7.36-7.30 (m, 2H), 7.28-7.23 (m, 3H), 7.10 (t,  $J = 8$  Hz, 1H), 7.00 (d,  $J = 8.4$  Hz, 1H), 6.61 (s, 1H), 5.27 (s, 2H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 145.8, 135.3, 130.6, 130.0, 129.2, 128.4, 128.3, 128.1, 127.0, 126.0, 122.8, 120.9, 76.2; IR (KBr)  $\nu_{\text{max}}$ : 3025.2, 2859.4, 1669.1, 1487.4, 1205.0, 1062.4, 1015.7, 853.2, 768.8, 687.0, 512.2  $\text{cm}^{-1}$ ; MS (ESI): 302.10 ( $\text{M}+\text{H}$ ) $^+$ ; Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{ClNOS}$ : C, 63.68; H, 4.01; N, 4.64. Found: C, 63.76; H, 4.11; N, 4.76.

**(Z)-N-((Z)-4-benzylidene-1,3-oxathiolan-2-ylidene)-2-methylaniline (5nb):** 96 mg, 82% yield; white solid;  $^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.25 (m, 2H), 7.25-7.12 (m, 4H), 7.10-7.00 (m, 2H), 6.90-6.83 (m, 1H), 6.58 (s, 1H), 5.21 (s, 2H), 2.21 (s, 3H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  161.1, 147.0, 130.7, 130.4 (31.5 Hz), 129.5 (52.5 Hz), 128.6 (31.5 Hz), 127.8 (48.8 Hz), 126.6 (44.3 Hz), 124.6, 120.4, 120.0, 100.8, 75.2, 17.8; IR (KBr)  $\nu_{\text{max}}$ : 3005.2, 2859.9, 1599.1, 1457.4, 1205.0, 1062.4, 1015.0, 855.2, 768.8, 657.7, 502.2  $\text{cm}^{-1}$ ; MS (ESI): 281.70 ( $\text{M}+\text{H}$ ) $^+$ ; Anal. Calcd for  $\text{C}_{17}\text{H}_{15}\text{NOS}$ : C, 72.57; H, 5.37; N, 4.98. Found: C, 72.52; H, 5.43; N, 5.08.

**(Z)-N-((Z)-4-benzylidene-1,3-oxathiolan-2-ylidene)-4-(tert-butyl)aniline (5nc):** 82 mg, 86% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.33 (m, 5H), 7.28-7.24 (m, 2H), 6.92 (d,  $J = 8.4$  Hz, 2H), 6.60 (s, 1H), 5.18 (d,  $J = 1.6$  Hz, 2H), 1.33 (s, 9H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 147.4, 145.3, 135.0, 130.4, 128.5, 127.8, 127.0, 125.7, 120.8, 120.0, 74.7, 34.4, 31.4; IR (KBr)  $\nu_{\text{max}}$ : 3025.2, 2859.2, 1669.1, 1457.4, 1205.2, 1062.4, 1065.7, 851.2, 768.8, 697.0, 512.2  $\text{cm}^{-1}$ ; MS (ESI): 324.30 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{20}\text{H}_{21}\text{NOS}$ : C, 74.27; H, 6.54; N, 4.33. Found: C, 74.31; H, 6.50; N, 4.27.

**(Z)-N-((Z)-4-benzylidene-1,3-oxathiolan-2-ylidene)-2-methoxyaniline (5nd):** 76 mg, 71% yield; pale yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.27 (m, 2H), 7.26-7.10 (m, 4H), 6.95-6.93 (m, 3H), 6.57 (s, 1H), 5.23 (d,  $J = 1.6$  Hz, 2H), 3.83 (s, 3H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 151.7, 137.8, 135.5, 130.7, 129.2, 128.3, 126.0, 122.6, 121.4, 120.3, 119.8, 112.2, 75.8, 56.2; IR (KBr)  $\nu_{\text{max}}$ : 3005.2, 2859.1, 1729.1, 1787.4, 1265.0, 1060.4, 1019.7, 853.2, 738.8, 687.0, 502.9  $\text{cm}^{-1}$ ; MS (ESI): 298.20 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{S}$ : C, 68.66; H, 5.08; N, 4.71. Found: C, 68.55; H, 5.01; N, 4.65.

**(Z)-N-((Z)-4-benzylidene-1,3-oxathiolan-2-ylidene)-3-methoxyaniline (5ne):** 79 mg, 73% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.24 (m, 6H), 6.70 (dd,  $J = 2.0, 1.6$  Hz, 1H), 6.60-6.56 (m, 2H), 6.55 (s, 1H), 5.20 (d,  $J = 1.6$  Hz, 2H), 3.80 (s, 3H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5, 149.6, 153.0, 130.1, 129.6, 129.0, 127.9, 120.3, 115.3, 113.6, 110.5, 108.7, 107.1, 75.1, 55.4; IR (KBr)  $\nu_{\text{max}}$ : 3055.2, 2899.4, 1869.1, 1487.4, 1225.0, 1062.4, 1045.7, 853.2, 768.8, 667.0, 502.6  $\text{cm}^{-1}$ ; MS (ESI): 298.20 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{S}$ : C, 68.66; H, 5.08; N, 4.71. Found: C, 68.55; H, 5.01; N, 4.65.

**(Z)-4-(tert-butyl)-N-((Z)-4-(4-nitrobenzylidene)-1,3-oxathiolan-2-ylidene)aniline (5oc):** 117 mg, 92% yield; yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22-8.20 (d,  $J = 8.4$  Hz, 2H), 7.45-7.35 (m, 4H), 6.97-6.95 (d,  $J = 8.4$  Hz, 2H), 3.84 (s, 2H), 1.32 (s, 9H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 142.6, 142.3, 140.5, 138.9, 127.8, 124.4, 121.4, 119.0, 115.3, 112.5, 29.4, 27.5, 26.4; IR (KBr)  $\nu_{\text{max}}$ : 3015.2, 2659.4, 1969.1, 1487.4, 1205.1, 1062.4, 1023.7, 853.0, 768.8, 681.0, 512.9  $\text{cm}^{-1}$ ; MS (ESI): 369.12 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$ : C, 65.20; H, 5.47; N, 7.60. Found: C, 55.56; H, 3.57; N, 4.15.

**General procedure for synthesis of 3,4-disubstituted (E)-N-(Z)-4-ethylidene-1,3-oxathiolan-2-ylidenes.**

**(Z)-2-chloro-N-((Z)-4-(4-nitrobenzylidene)-1,3-oxathiolan-2-ylidene)aniline (5oa):** To a solution of **1o** (120 mg, 0.799 mmol) in ACN (1.2 mL) was added successively 1-chloro-2-isothiocyanato-benzene (**2a**) (135.1 mg, 0.799 mmol) and DBU (121.7 mg, 0.799 mmol) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for about 1 hr and then quenched into ice-water (25 mL), extracted with MTBE (25 mL), and the organic layer washed with brine solution (25 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Then the filtrate was stirred along with silica gel (500 mg) for 0.5 hr, filtered and concentrated at a reduced pressure to give 229.6 mg, 90% yield; yellow solid. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) δ 8.22-8.20 (d, *J* = 8.4 Hz, 2H), 7.43-7.39 (m, 3H), 7.28-7.21 (m, 1H), 7.09-7.00 (m, 2H), 6.78 (s, 1H), 3.85 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 164.1, 147.4, 145.5, 143.7, 133.2, 130.4, 129.4, 127.9, 126.5, 125.6, 124.1, 121.4, 118.3, 32.3; IR (KBr)  $\nu_{\max}$ : 3022.2, 2859.0, 1669.1, 1481.4, 1205.0, 1102.4, 1195.7, 853.2, 768.8, 667.0, 509.2 cm<sup>-1</sup>; MS (ESI): 347.02 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>16</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>3</sub>S: C, 55.41; H, 3.20; N, 8.08. Found: C, 55.82; H, 3.51; N, 8.42.

**(Z)-2-chloro-N-((Z)-4-(2,3-difluorobenzylidene)-1,3-oxathiolan-2-ylidene)aniline (5pa):** 94 mg, 87% yield; light brown solid; <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.26-7.22 (m, 1H), 7.11-7.00 (m, 5H), 6.75 (s, 1H), 5.32 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 162.7, 152.0, 149.4, 146.8, 145.3, 134.0, 130.0, 127.2, 125.8, 125.3, 124.3, 123.1, 122.5, 116.7, 111.5, 75.8; IR (KBr)  $\nu_{\max}$ : 3029.2, 2959.4, 1769.1, 1487.4, 1185.0, 1062.4, 1015.7, 853.1, 768.5, 687.0, 522.2 cm<sup>-1</sup>; MS (ESI): 338.10 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>16</sub>H<sub>10</sub>ClF<sub>2</sub>NOS: C, 56.89; H, 2.98; N, 4.15. Found: C, 56.96; H, 2.91; N, 4.05.

**(Z)-2-chloro-N-((Z)-4-(5-chloro-2-methoxybenzylidene)-1,3-oxathiolan-2-ylidene)aniline (5qa):** 79 mg, 77% yield; yellow solid; <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) δ 7.40 (d, *J* = 6 Hz, 1H), 7.26-7.10 (m, 4H), 7.10-6.97 (m, 1H), 6.78 (d, *J* = 8 Hz, 2H), 5.26 (s, 2H), 3.82 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 179.5, 155.8, 133.1, 132.9, 132.2, 131.4, 131.0, 130.8, 130.5, 130.1, 128.6, 128.1, 125.2, 124.3, 111.6, 55.6, 24.1; IR (KBr)  $\nu_{\max}$ : 3005.2, 2009.4, 1869.1, 1487.4, 1205.0, 1062.4, 1015.7, 853.2, 768.8, 687.6, 504.2 cm<sup>-1</sup>; MS

(ESI): 366.20 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>17</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub>S: C, 55.75; H, 3.58; N, 3.82. Found: C, 55.83; H, 3.69; N, 3.92.

**(Z)-2-chloro-N-((Z)-4-(5-chloro-2-methylbenzylidene)-1,3-oxathiolan-2-ylidene)aniline (5ra):** 89 mg, 83% yield; pale yellow solid; <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) δ 7.40 (d, *J* = 8 Hz, 1H), 7.26-7.20 (m, 1H), 7.14-7.05 (m, 4H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 5.26 (d, *J* = 1.2 Hz, 2H), 2.25 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 161.1, 147.2, 136, 134.6, 133.3, 131.8, 131.6, 130.1, 128.0, 127.7, 126.9, 126.5, 125.7, 122.2, 117.7, 74.6, 19.3; IR (KBr)  $\nu_{\text{max}}$ : 3033.2, 2599.0, 1669.1, 1481.4, 1205.0, 1092.4, 1095.7, 853.2, 768.1, 667.0, 500.2 cm<sup>-1</sup>; MS (ESI): 350.40 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>17</sub>H<sub>13</sub>Cl<sub>2</sub>NOS: C, 58.29; H, 3.74; N, 4.00. Found: C, 58.33; H, 3.79; N, 4.10.

**(Z)-2-chloro-N-((Z)-4-(4-methylbenzylidene)-1,3-oxathiolan-2-ylidene)aniline (5sa):** 71.9 mg, 88% yield; yellow solid; <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.43 (m, 1H), 7.28-7.01 (m, 7H), 6.61 (s, 1H), 5.28 (s, 2H), 2.35 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 130.9, 125.1, 123.1, 122.4, 121.5, 120.9, 120.6, 119.6, 118.5, 115.4, 113.4, 68.7, 14.2; IR (KBr)  $\nu_{\text{max}}$ : 3092.2, 2659.0, 1969.1, 1501.4, 1205.0, 1082.4, 1195.5, 893.2, 748.8, 667.0, 529.2 cm<sup>-1</sup>; MS (ESI): 316.10 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>17</sub>H<sub>14</sub>ClNOS: C, 64.65; H, 4.47; N, 4.44. Found: C, 65.02; H, 4.56; N, 4.76.

**(Z)-N-((Z)-4-(5-chloro-2-methylbenzylidene)-1,3-oxathiolan-2-ylidene)-2-methoxyaniline (5td):** 88 mg, 89% yield; yellow solid; <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) δ 7.16-7.09 (m, 4H), 6.92 (t, *J* = 6, 2.4 Hz, 3H), 6.57 (s, 1H), 5.22 (d, *J* = 1.6 Hz, 2H), 3.83 (s, 3H), 2.24 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 146.1, 151.1, 137.1, 136.2, 134.6, 133.9, 131.8, 131.5, 127.9, 126.9, 125.7, 121.8, 121.0, 117.1, 111.8, 74.7, 55.7, 19.3; IR (KBr)  $\nu_{\text{max}}$ : 3059.2, 2759.4, 1589.1, 1407.4, 1185.0, 1062.4, 1015.7, 853.1, 778.5, 687.0, 505.5 cm<sup>-1</sup>; MS (ESI): 346.10 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>18</sub>H<sub>16</sub>ClNO<sub>2</sub>S: C, 62.51; H, 4.66; N, 4.05. Found: C, 62.42; H, 4.56; N, 4.01.

**(Z)-2-chloro-N-((Z)-4-((5-methylpyridin-2-yl)methylene)-1,3-oxathiolan-2-ylidene)aniline (5ua):** 79 mg, 81% yield; semi yellow solid; <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) δ 8.39 (s, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.24-7.23

(m, 1H), 7.10-7.00 (m, 3H), 6.56 (s, 1H), 5.32 (s, 2H), 2.29 (s, 3H);  $^{13}\text{C}$  {1H} NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 150.6, 149.6, 145.9, 137.5, 134.8, 131.4, 130.4, 128.0, 127.1, 125.6, 123.6, 123.0, 116.8, 75.2, 18.7; IR (KBr)  $\nu_{\text{max}}$ : 3019.2, 2959.4, 1769.7, 1467.4, 1085.0, 1042.4, 1005.7, 823.1, 768.5, 687.8, 500.2  $\text{cm}^{-1}$ ; MS (ESI): 317.30 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{OS}$ : C, 60.66; H, 4.14; N, 8.84. Found: C, 60.77; H, 4.21; N, 8.91.

**General procedure for synthesis of 3-substituted 4-methylene-oxazolidine-2-thiones (6a-6e).**

**4-methylene-3-phenyloxazolidine-2-thione (6a):** To a solution of prop-2-yn-1-ol (180 mg, 0.321 mmol) in ACN (1.2 mL) was added successively 1-chloro-2-isothiocyanato-benzene (**2a**) (433 mg, 0.321 mmol) and DBU (500 mg, 0.321 mmol) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for about 1 hr and then quenched into ice-water (25 mL), extracted with MTBE (25 mL), and the organic layer washed with brine solution (25 mL), dried over  $\text{Na}_2\text{SO}_4$  and filtered. Then the filtrate was stirred along with silica gel (500 mg) for 0.5 hr, filtered and concentrated at a reduced pressure to give 400 mg, 65% yield; semi yellow solid;  $^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.47 (m, 3H), 7.33-7.26 (m, 2H), 5.29 (t,  $J = 5.1$  Hz, 2H), 4.28 (q,  $J = 2.7$  Hz, 1H), 4.09 (q,  $J = 2.7$  Hz, 1H);  $^{13}\text{C}$  {1H} NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  188.7, 143.9, 135.0, 129.9, 129.4, 128.1, 84.4, 71.6; IR (KBr)  $\nu_{\text{max}}$ : 3013.2, 2859.4, 1869.1, 1407.4, 1185.0, 1062.4, 1015.7, 833.1, 768.5, 687.0, 512.2  $\text{cm}^{-1}$ ; MS (ESI): 192.00 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{10}\text{H}_9\text{NOS}$ : C, 62.80; H, 4.74; N, 7.32. Found: C, 61.70; H, 4.42; N, 7.42.

**3-(4-(benzyloxy)phenyl)-4-methyleneoxazolidine-2-thione (6b):** 72 mg, 76% yield; semi solid;  $^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.35 (m, 5H), 7.26-7.7.20 (m, 2H), 7.13-7.10 (m, 2H), 5.27 (t,  $J = 5.1$  Hz, 2H), 5.10 (s, 2H), 4.27 (q,  $J = 2.5$  Hz, 1H), 4.10 (q,  $J = 2.5$  Hz, 1H);  $^{13}\text{C}$  {1H} NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  185.0, 159.3, 144.1, 136.4, 129.2, 128.7, 128.2, 127.6, 116.0, 84.3, 71.5, 70.4; IR (KBr)  $\nu_{\text{max}}$ : 3023.2, 2019.4, 1969.1, 1407.4, 1195.0, 1062.0, 1015.7, 853.2, 768.2, 687.6, 500.2  $\text{cm}^{-1}$ ; MS (ESI): 298.20 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{S}$ : C, 68.66; H, 5.08; N, 4.71. Found: C, 68.55; H, 5.17; N, 4.76.

**4-methylene-3-(o-tolyl)oxazolidine-2-thione (6c):** 75 mg, 80% yield; semi yellow solid;  $^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.34 (m, 3H), 7.16 (m, 1H), 5.31 (t,  $J = 4.8$  Hz, 2H), 4.26 (t,  $J = 4.8$  Hz, 1H), 3.90 (t,  $J = 4.8$

Hz, 1H), 2.21 (s, 3H);  $^{13}\text{C}$  {1H} NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  188.0, 143.0, 136.4, 133.4, 131.8, 131.6, 130.3, 129.9, 128.4, 127.9, 127.6, 127.5, 84.3, 71.7, 17.4; IR (KBr)  $\nu_{\text{max}}$ : 3025.2, 2009.4, 1669.1, 1487.4, 1205.0, 1062.1, 1015.7, 853.2, 798.8, 657.6, 509.9  $\text{cm}^{-1}$ ; MS (ESI): 206.10 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{11}\text{H}_{11}\text{NOS}$ : C, 64.36; H, 5.40; N, 6.82. Found: C, 64.25; H, 5.32; N, 6.91.

**3-(4-(tert-butyl)phenyl)-4-methyleneoxazolidine-2-thione (6d)**: 85 mg, 70% yield; semi yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (dd,  $J = 2$  Hz, 2H), 7.24 (dd,  $J = 2$  Hz, 2H), 5.27 (t,  $J = 4.8$  Hz, 2H), 4.26 (t,  $J = 5.2$  Hz, 1H), 4.13 (t,  $J = 5.2$  Hz, 1H), 1.36 (s, 9H);  $^{13}\text{C}$  {1H} NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  188.8, 152.4, 144.1, 132.2, 127.4, 126.8, 84.4, 71.5, 31.3; IR (KBr)  $\nu_{\text{max}}$ : 3020.2, 2009.4, 1839.1, 1497.4, 1205.0, 1022.1, 1015.7, 856.1, 768.8, 687.6, 510.7  $\text{cm}^{-1}$ ; MS (ESI): 248.20 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{14}\text{H}_{17}\text{NOS}$ : C, 67.98; H, 6.93; N, 5.66. Found: C, 68.08; H, 7.02; N, 5.71.

**3-(2-methoxyphenyl)-4-methyleneoxazolidine-2-thione (6e)**: 70 mg, 60% yield; semi yellow solid;  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.44 (m, 1H), 7.26-7.22 (m, 1H), 7.11-7.07 (m, 2H), 5.34-5.24 (m, 2H), 4.22 (q,  $J = 7.2$  Hz, 1H), 3.95 (q,  $J = 7.2$  Hz, 1H), 3.84 (s, 3H);  $^{13}\text{C}$  {1H} NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.9, 155.1, 143.2, 131.2, 129.9, 123.2, 121.4, 112.9, 83.7, 71.8, 55.9; IR (KBr)  $\nu_{\text{max}}$ : 3031.2, 2079.4, 1869.0, 1527.4, 1205.0, 1032.4, 1002.7, 873.2, 768.8, 685.6, 501.0  $\text{cm}^{-1}$ ; MS (ESI): 222.10 (M+H) $^+$ ; Anal. Calcd for  $\text{C}_{11}\text{H}_{11}\text{NO}_2\text{S}$ : C, 59.71; H, 5.01; N, 6.33. Found: C, 59.88; H, 5.18; N, 6.39.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Characterization data, copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  {1H} NMR spectra and experimental procedure.

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No special mention is required regarding the author contributions.

### Notes

The authors declare no competing financial interest.

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