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Direct Access to 2-Thioxooxazolidin-4-ones and Oxazolidine-2,4-diones from α-Keto Thioesters through Thiolate Transfer

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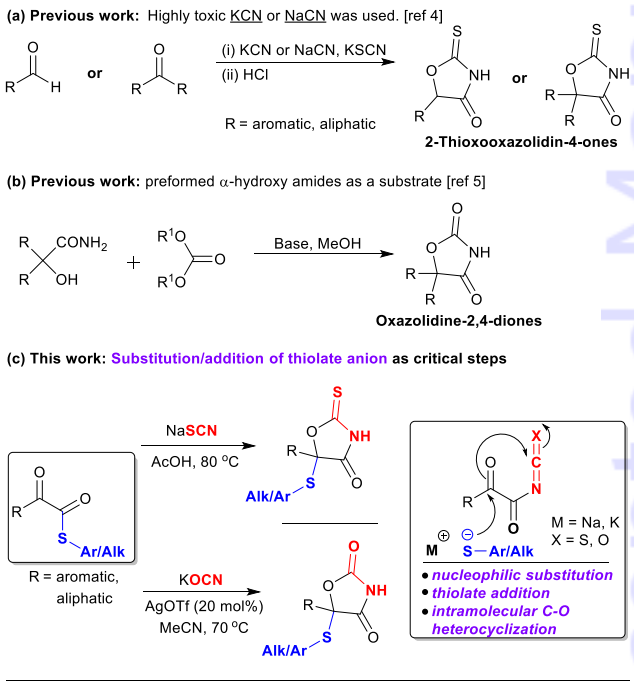
Abstract. We report a direct synthesis of 2-thioxooxazolidin-4-ones and oxazolidine-2,4-diones from α-keto thioesters with sodium thiocyanate or potassium cyanate, respectively. The reactions proceed through nucleophilic substitution of a thioester with thiocyanate/cyanate anion, thiolate anion addition to carbonyl carbon, and subsequent intramolecular C-O heterocyclization.

Keywords: α-keto thioesters; oxazolidine-2,4-diones; rearrangement; synthetic methods; 2-thioxooxazolidin-4-ones;

2-Thioxooxazolidin-4-one[1] and oxazolidine-2,4-dione[2] derivatives are important synthetic intermediates and have found widespread applications in medicinal chemistry. For example, 2-thioxooxazolidin-4-one derivatives were used for the synthesis of (5-phenyl-4-oxo-2-oxazolin-2-yl)piperazine derivatives, which show promising antimalarial activity against *Plasmodium berghei* in mice.[1a] On the other hand, a variety of anticonvulsant drugs including dimethadione, ethadione, paramethadione, and trimethadione have the oxazolidine-2,4-dione skeleton as the core structure.[3] However, there is a lack of general methods to access them. Among the few methods available for synthesizing 2-thioxooxazolidin-4-ones, the reaction of a carbonyl compound with an aqueous solution of potassium thiocyanate and potassium cyanide or sodium cyanide in acetone, followed by hydrolysis with hydrochloric acid is more common.[1,4] However, this method suffers from certain drawbacks, such as utilization of the highly toxic KCN or NaCN, and limited substrate scope (Scheme 1a). On the other hand, the synthesis of oxazolidine-2,4-diones mainly depends upon the condensation of dialkyl carbonates with an amide of the appropriately substituted α-hydroxy acids in the presence of a base (Scheme 1b).[2,5] However, this method requires preformed α-hydroxy amides as a substrate which are sometimes difficult to make. Thus, the development of an efficient route for the synthesis of 2-thioxooxazolidin-4-ones and oxazolidine-2,4-diones from readily accessible starting materials will be a valuable contribution to this field.



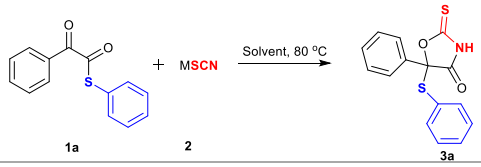
Scheme 1. Synthesis of 2-thioxooxazolidin-4-ones and oxazolidine-2,4-diones.

Thiocyanate and cyanate salts have been recognized as one of the most efficient and versatile reagents for accessing diverse heterocycles.[6] In the course of our continuing efforts,[7] the reactivity of α-keto thioesters with these salts was investigated. We observed that α-keto thioesters underwent nucleophilic displacement with thiocyanate/cyanate on the thioester carbonyl, followed by intermolecular thiolate addition to the carbonyl carbon, and subsequent intramolecular C-O heterocyclization to

afford 2-thioxooxazolidin-4-one and oxazolidine-2,4-dione derivatives, respectively (Scheme 1c).

To optimize the reaction conditions for 2-thioxooxazolidin-4-ones, we initiated model studies with α-keto thioester **1a** and NaSCN **2a** at 80 °C in various solvents such as DMSO, CH_3CN, trifluoroacetic acid, formic acid, and water (entries 1-5, Table 1). However, the product **3a** was formed

Table 1. Optimization of the reaction conditions for 2-thioxooxazolidin-4-ones.[a]



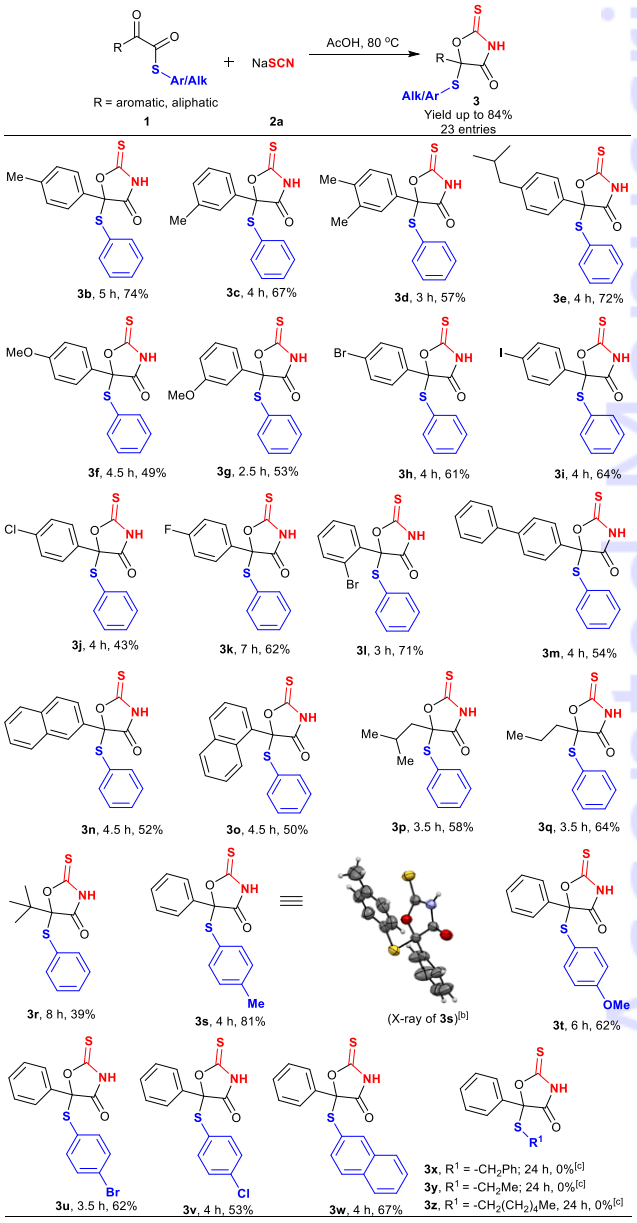
Entry	MSCN (equiv)	Solvent	Time (h)	Yield (%)
1	NaSCN (2)	DMSO	5	35
2	NaSCN (2)	CH_3CN	5	51
3	NaSCN (2)	CF_3COOH	3	21
4	NaSCN (2)	HCOOH	5	40
5	NaSCN (2)	H_2O	12	n.d.[b]
6	NaSCN (2)	MeOH	1	n.d.[c]
7	**NaSCN (2)**	**AcOH**	**4**	**84**
8	KSCN (2)	AcOH	4	59
9	NH_4SCN (2)	AcOH	4	56
10	AgSCN (2)	AcOH	10	n.d.[b]
11	CuSCN (2)	AcOH	10	n.d.[b]
12	$Co(SCN)_2$ (2)	AcOH	10	n.d.[b]
13	KSCN (2)	AcOH	3	48[d]
14	NaSCN (2)	AcOH	3	53[d]
15	NaSCN (2)	AcOH	3	40[e]
16	NaSCN (2)	AcOH	3	40[f]
17	NaSCN (2)	AcOH	3	37[g]
18	NaSCN (2)	AcOH	4	40[h]
19	NaSCN (3)	AcOH	3	53
20	NaSCN (1.2)	AcOH	8	48
21	NaSCN (2)	-	12	n.d.[b]

[a] *Reaction conditions*: **1a** (0.03 g, 0.124 mmol) and MSCN **2** (2.0 equiv/mmol) were heated in 0.3 mL solvent at 80 °C, employing time as noted; yields are of isolated products after purification.
[b] n.d. = product not detected; Starting materials isolated.
[c] Heated to 60 °C; n.d. = product not detected; isolated $PhCOCO_2Me$ in 79% yield.
[d] AgOAc (10 mol %) was used.
[e] $AgBF_4$ (10 mol %) was used.
[f] $AgPF_6$ (10 mol %) was used.
[g] AgOTf (10 mol %) was used.
[h] Ag_2CO_3 (10 mol %) was used.

either in low to moderate yields or only starting materials were recovered. The use of MeOH as a solvent also failed to deliver the required product **3a** (entry 6); methyl benzoylformate ($PhCOCO_2Me$) was obtained instead in good yield. To our delight, the utilization of AcOH as a solvent could significantly improve the yield to 84% (entry 7). A screening of other commercially available thiocyanate sources such as KSCN, NH_4SCN, AgSCN, CuSCN, and $Co(SCN)_2$ provided inferior results (entries 8-12, Table 1). Different silver salts such as AgOAc, $AgBF_4$, $AgPF_6$, AgOTf, and Ag_2CO_3 were also screened (entries 13-18), but without success. The amount of NaSCN appeared to be crucial. Increasing the amount to 3.0 equiv or decreasing to 1.2 equiv only lowered the yield (entries 19-20). But in the absence of any solvent the reaction did not proceed at all (entry 21).

With the optimized reaction conditions, we started to explore the substrate scope and generality for this transformation (Table 2). In general, the reaction is

Table 2. Substrate scope for α-keto thioesters and thiocyanates.[a]



[a] *Reaction conditions*: α-Keto thioeseter **1** (0.05 g, 1 equiv) and NaSCN **2a** (2 equiv/mmol) in AcOH (0.5 mL) at 80 °C; yields are of isolated products.
[b] The thermal ellipsoids are shown in 50% probability level.

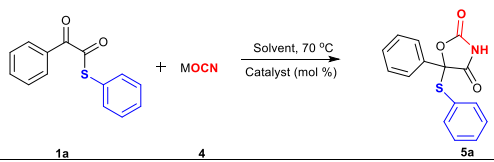
[c] With unreacted starting materials, minor unidentified spots were detected.

tolerant to variation in substituents in the aryl group at the α-position of the α-keto thioesters. Substrates containing an aromatic ring with electron-donating (**1b-g**) or withdrawing substituents (**1h-l**) worked well and delivered the corresponding products in moderate to good yields (**3a-l**). Furthermore, replacement of the aryl group with a biphenyl (**1m**) or fused aryl ring (**1n-o**) delivered the corresponding products in moderate yields (**3m-o**). It is noteworthy that the α-keto thioester having an alkyl group at the α-position (**1p-r**) were also found to be reactive under the reaction conditions and furnished the products in moderate yields (**3p-r**).

We next turned our attention to assess the scope of this reaction by varying the thiol substituents in α-keto thioesters from –SPh to substituted aromatic thiols or aliphatic thiols. As indicated in Table 2, electron-donating (**1s-t**) or electron-withdrawing (**1u-v**) substituents in the aromatic ring or a naphthyl substituent (**1w**) were well-tolerated and produced the expected products in moderate to good yields (**3s-w**). However, α-keto thioesters bearing short-chain aliphatic thiols such as benzyl and ethyl (**1x-y**) or longer alkyl chain such as hexyl (**1z**) did not undergo any such cyclization, perhaps due to the lower stability of the *in-situ* generated thiolate anion in acidic solution. The structure of **3s** was established by single crystal X-ray diffraction analysis (Table 2).[8] Replacement of the α-keto thioester with α-keto oxoester did not result in any expected product, ostensibly owing to the stronger C-O bond in oxoester and hence less reactive compared to the C-S bond in thioesters.

Next, we examined the scope of the reaction for α-keto thioesters with cyanate salts **4** (Table 3). Under the standard reaction conditions described in Table 2 for the formation of 2-thioxooxazolidin-4-ones, **1a** did not undergo any cyclization with cyanate salts to

Table 3. Optimization of the reaction conditions for oxazolidine-2,4-diones.[a]



Entry	MOCN (equiv)	Catalyst (mol %)	Solvent	Time (h)	Yield[b] (%)
1	NaOCN (2)	-	AcOH	12	n.d.[c,d]
2	KOCN (2)	-	AcOH	12	n.d.[c,d]
3	**KOCN (2)**	**AgOTf (20)**	**MeCN**	**11**	**70**
4	NaOCN (2)	AgOTf (20)	MeCN	24	28[e]
5	KOCN (2)	AgOTf (10)	MeCN	21	55

[a] *Reaction conditions*: **1a** (0.03 g, 0.124 mmol), MOCN **4** (equiv/mmol), and catalyst (if needed) were heated in 1.0 mL solvent at 70 °C, employing time as noted.

[b] Yields are of isolated products after purification.

[c] Heated to 80 °C with 0.3 mL AcOH.

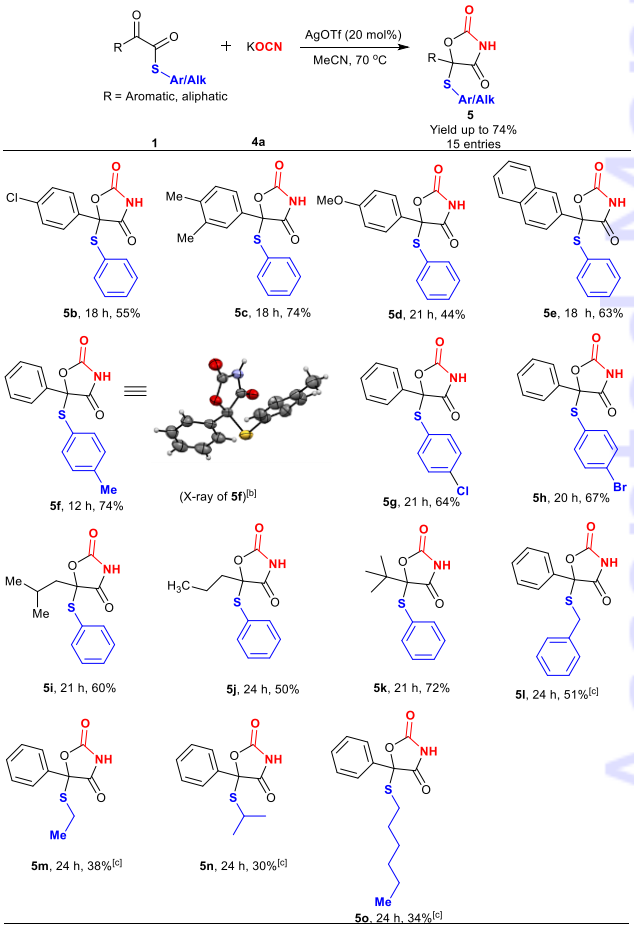
[d] n.d. = not detected

[e] Starting materials were present.

produce oxazolidine-2,4-diones (entries 1-2, Table 3). This might be ascribed to the nitrogen atom of a cyanate anion being less nucleophilic than that of a thiocyanate anion. However, in the presence of Ag-catalyst, which may form a complex by coordinating with sulphur atom, nucleophilic attack of a cyanate anion on the thioester carbonyl will be facilitated, resulting in the formation of the desired oxazolidine product. After optimization with different cyanate salts, catalysts, and solvents (Table 3), use of KOCN and 20 mol% AgOTf in acetonitrile at 70 °C proved to be optimal (see also the Supporting Information for optimization studies).

As indicated in Table 4, the reactions worked well with electron-poor, electron-rich, or naphthyl substituted α-keto thioesters and produced the oxazolidine-2,4-dione derivatives in moderate to good yields (**5b-h**). An alkyl group at the α-position

Table 4. Substrate scope for α-keto thioesters and cyanates.[a]



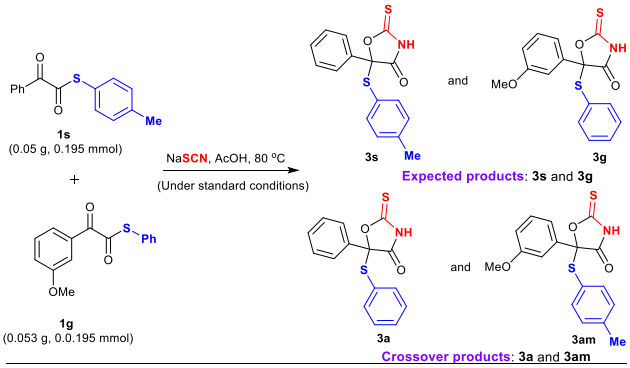
[a] *Reaction conditions*: α-Keto thioeseter **1** (0.05 g, 1 equiv), KOCN **4a** (2 equiv/mmol), AgOTf (20 mol %) in acetonitrile (1.5 mL) at 70 °C, employing time as noted; yields are of isolated products.

[b] The thermal ellipsoids are shown in 50% probability level.

[c] Some starting materials were recovered.

of keto thioesters also furnished the products (**5i-k**). Substrates bearing aliphatic thiols were also found to react under these conditions, delivering the products in moderate yields (**5l-o**, Table 4). It is interesting to note that α-keto thioesters **1x-z** did not give the desired products with NaSCN/AcOH, with or without catalyst (Table 2). However, similar thioesters afforded the corresponding products **5l-o** with KOCN in presence of catalytic AgOTf (Table 4). It is possible that AgOTf is responsible for stabilizing the aliphatic thiolate anion generated *in situ*, though the exact reason is not very clear at this moment. The structure of **5f** was established by a single crystal X-ray diffraction analysis (Table 4).[8]

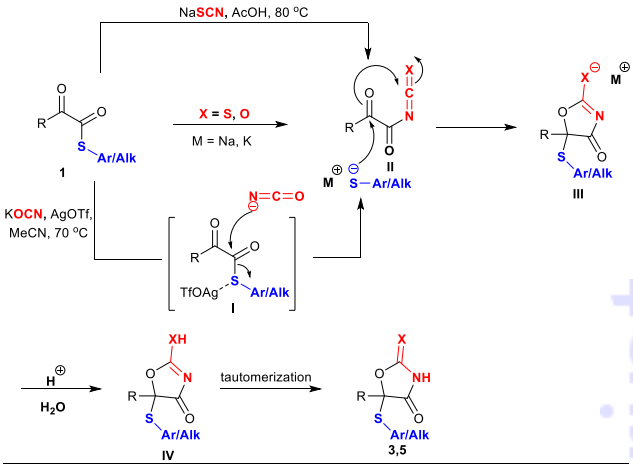
To gain some mechanistic insight, crossover experiment for 2-thioxooxazolidin-4-one derivatives were carried out (Scheme 2). An equimolar mixture of **1s** and **1g** was treated with NaSCN in AcOH at 80 °C under standard conditions. It gave crossover products (**3a** and **3am**) in addition to the expected



Scheme 2. Crossover experiment.

products (**3s** and **3g**). This result suggested that the thiolate anion transfer[9] was intermolecular, thus supporting a stepwise mechanism for this reaction. The crossover experiment for oxazolidine-2,4-dione derivatives also confirmed the stepwise mechanism (see the Supporting Information).

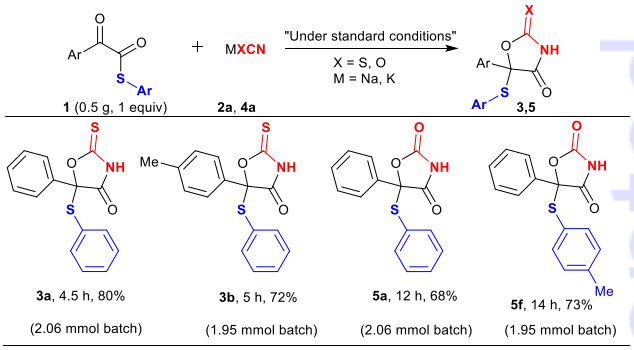
Based on the experimental results and control experiments, a plausible reaction mechanism is proposed in Scheme 3. We presume that initial nucleophilic attack of thiocyanate anion on the thioester carbonyl with simultaneous elimination of the thiolate anion could lead to intermediate **II**. On the other hand, in a cyanate reaction, Ag(I) may coordinate with sulphur atom of the α-keto thioester to form a complex **I**,[10] resulting in increase of the electrophilicity of thioester carbonyl centre, which undergoes substitution easily with less nucleophilic cyanate anion and elimination to generate **II**. Subsequent nucleophilic attack by the thiolate to the carbonyl carbon followed by intramolecular C-O heterocyclization would furnish intermediate **IV**, via intermediate **III**. Finally, intermediate **IV** undergoes rapid tautomerization to give the desired product (**3**,**5**).



Scheme 3. Proposed mechanistic pathway.

To highlight the practical usefulness of these syntheses, we successfully scaled up the reaction to 0.5 g of **1** and isolated **3a**, **3b**, **5a**, and **5f** respectively, without any significant diminution in the yields (Table 5).

Table 5. Scale-up batches.[a]

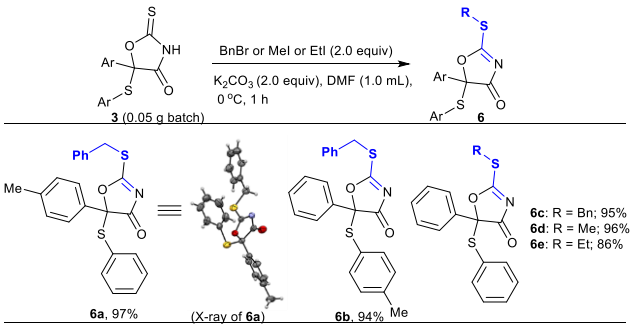


[a] Unless otherwise noted, all the reactions were carried out under the conditions in Table 2 and Table 4; Yields of **3,5** are of isolated products after purification.

The synthetic versatility of this work could be demonstrated by treating 2-thioxooxazolidin-4-one derivatives with alkyl bromide/iodide in the presence of K_2CO_3 as a base to isolate *S*-alkylated oxazol-4(5*H*)-one derivatives **6a-e** in excellent yields (Scheme 4).[11] The structure of **6a** was established by a single crystal X-ray diffraction analysis (Scheme 4).[8]

In summary, we have developed a general approach to 2-thioxooxazolidin-4-one derivatives from α-keto thioesters, NaSCN, and acetic acid. Direct access to oxazolidine-2,4-dione derivatives has

also been realized by AgOTf-catalyzed reaction of α-keto thioesters and KOCN in acetonitrile. Both the reactions proceed through the nucleophilic substitution, thiolate addition, and subsequent



Scheme 4. Synthetic applications.

intramolecular thiolate addition, and subsequent intramolecular C-O heterocyclization. To demonstrate the potentiality of 2-thioxooxazolidin-4-one derivatives, a base-mediated alkylation reaction of these derivatives has been performed, which shows that they offer efficient access to *S*-alkylated oxazol-4(5*H*)-ones. Further investigations with α-keto thioesters as synthetically useful building block are ongoing and will be reported in due course.

Experimental Section

Representative examples

5-Phenyl-5-(phenylthio)-2-thioxooxazolidin-4-one 3a: α-Keto thioester **1a** (0.05g, 0.206 mmol, 1.0 equiv) and sodium thiocyanate **2a** (0.033 g, 0.41 mmol, 2.0 equiv) was heated in acetic acid (0.5 mL) at 80 °C for 4 h. After completion of the reaction (TLC), saturated $NaHCO_3$ solution was added at 0 °C, and the mixture was extracted with ethyl acetate (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was purified by silica gel column chromatography [230–400; eluent:ethyl acetate/*n*-hexane] to obtain **3a**; R_f = 0.3; eluent, EtOAc/*n*-hexane (15%); isolated yield = 0.052 g, 84%; white solid; mp 139-141 °C. ^{1}H NMR (600 MHz, d_6-DMSO): δ = 13.54 (br. s., 1 H), 7.65 (d, *J* = 7.8 Hz, 2 H), 7.57 (d, *J* = 7.8 Hz, 2 H), 7.50 - 7.55 (m, 4 H), 7.46 ppm (t, *J* = 7.2 Hz, 2 H); ^{13}C NMR (150 MHz, d_6-DMSO): δ = 188.5, 171.7, 136.9 (2 CH), 132.7, 131.8, 130.7, 130.2 (2 CH), 129.7 (2 CH), 127.1, 125.7 (2 CH), 97.8 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 3112, 2901, 1777, 1474, 1321, 1207, 1000, 923, 871, 746, 690 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{15}H_{11}NO_2S_2$ $[M]^+$: 301.0231; found: 301.0236.

5-Phenyl-5-(phenylthio)oxazolidine-2,4-dione 5a: α-Keto thioester **1a** (0.05g, 0.206 mmol, 1.0 equiv), potassium cyanate **4a** (0.033 g, 0.41 mmol, 2.0 equiv), and AgOTf (0.01 g, 0.041 mmol, 0.2 equiv) was heated in CH_3CN (1.5 mL) at 70 °C under argon atmosphere for 11 h. After completion of the reaction (TLC), ethyl acetate was added into it. The solution was filtered through a Buchner funnel, saturated NH_4Cl solution was added into the filtrate, and the mixture was extracted with ethyl acetate (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was purified by silica gel column chromatography [230–400; eluent:ethyl acetate/*n*-hexane] to obtain **5a**; R_f = 0.3; eluent, EtOAc/*n*-hexane (17.5%); isolated yield = 0.041 g, 70%; white solid; mp 129-131 °C. ^{1}H NMR (600 MHz, d_6-DMSO): δ = 12.23 (br. s., 1 H), 7.68 (d, *J* = 7.8 Hz, 2 H), 7.57 (d, *J* = 7.8 Hz, 2 H), 7.54 (d, *J* = 7.2 Hz, 1 H), 7.46 - 7.51 ppm (m, 5 H); ^{13}C NMR (150 MHz, d_6-DMSO): δ = 171.4, 153.2, 136.9 (2 CH), 133.3, 131.6, 130.4, 130.2 (2 CH), 129.4 (2 CH), 127.5, 125.8 (2 CH), 94.5 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 3318, 1824, 1732, 1351, 1185, 1020, 971, 747, 691, 622 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{15}H_{11}NO_3S$ $[M]^+$: 285.0460; found: 285.0464.

2-(Benzylthio)-5-(phenylthio)-5-(*p*-tolyl)oxazol-4(5*H*)-one 6a: Dry K_2CO_3 (0.044 g, 0.316 mmol, 2.0 equiv) was added to a well-stirred solution of 2-thioxooxazolidin-4-one **3b** (0.05 g, 0.158 mmol, 1.0 equiv) in dry DMF (1.0 mL) under argon atmosphere at 0 °C. The reaction mixture was stirred for 10 min. Benzyl bromide (0.04 mL, 0.316 mmol, 2.0 equiv) was then added dropwise via syringe at that same temperature. After completion of the reaction (TLC), saturated NH_4Cl solution was added, and the mixture was extracted with ethyl acetate (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was purified by silica gel column chromatography [230–400; eluent:ethyl acetate/*n*-hexane] to obtain **6a**; R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); isolated yield = 0.062 g, 97%; white solid; mp 119-121 °C. ^{1}H NMR (600 MHz, d_6-DMSO): δ = 7.46 (t, *J* = 7.2 Hz, 1 H), 7.43 (d, *J* = 7.8 Hz, 2 H), 7.35 - 7.37 (m, 3 H), 7.32 - 7.34 (m, 6 H), 7.24 (d, *J* = 7.8 Hz, 2 H), 4.43 (q, *J* = 13.8, 18.0 Hz, 2 H), 2.30 ppm (s, 3 H); ^{13}C NMR (150 MHz, d_6-DMSO): δ = 193.8, 182.7, 140.1, 136.5 (2 CH), 136.4, 131.4, 130.1, 130.0 (4 CH), 129.4 (2 CH), 129.2 (2 CH), 128.3, 127.5, 125.7 (2 CH), 97.5, 35.6 (CH_2), 21.2 ppm; IR (KBr): $\tilde{\nu}_{max}$ = 2924, 1753, 1488, 1254, 1212, 1013, 951, 807, 753, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{23}H_{19}NO_2S_2Na$ $[M + Na]^+$: 428.0755; found: 428.0749.

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