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One-pot synthesis of 4-arylidene imidazolin-5-ones by reaction of amino acid esters with isocyanates and α-bromoketones†

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A simple and new multicomponent reaction for the one-pot synthesis of substituted 4-arylidene imidazolin-5-ones from L-amino acid methyl esters, iso-, isothio- or isoselenocyanates, and α-bromoketones is demonstrated. Isolation of thiohydantoin and 5-benzylidene 2-thioxoimidazolidin-4-one intermediates revealed a possible reaction mechanism. The strategy was further extended to the synthesis of 2-iminothiazolines and 2-thioxoimidazolin-4-ones.

Introduction

4-Arylidene imidazolones constitute the main core of green fluorescent proteins.[1] These fluorescent proteins (FPs) are an important imaging tool for studying various biological phenomenons.[2] Although various analogous FPs such as Kaede and BODIPY-like FPs are present, the arylidene imidazolone is found to be a common core within them.[3] Moreover, 4-aryl(alkyl)ated imidazolones exhibit a broad spectrum of bioactivities, such as anti-inflammatory,[4] cytotoxic,[5] and antibacterial and antifungal[6] activities.

Despite being a versatile scaffold, only a few synthetic methods for the preparation of these compounds are available in the literature (Fig. 1). For example, Lerestif reported obtaining substituted 4-yliden-2-imidazolin-5-ones through a 1,3-dipolar cycloaddition of imidate ylides and imino-alcohols in 1995.[7] Kojima and co-workers accomplished a synthetic sequence that contained preparation of Erlenmeyer azlactones from *N*-acetylglycine and aldehydes, and reacting them with amines to afford imidazolones.[8] Wu disclosed a four-step reaction with formation of 2-azidoacetamides from amides followed by a Staudinger-type cyclization to yield imidazolones, which were further condensed with aldehydes to afford 4-arylideneimidazolin-5-ones.[3b] Gabillet developed a phosphine-catalyzed tandem reaction consisting of umpolung addition of amidines to arylpropiolates followed by an intramolecular cyclization to yield 4-arylidene-5-imidazolones.[9]

Recently, Muselli achieved the synthesis of substituted 4-benzylidene imidazolones in two steps, comprising of condensation of an amido isocyanide with an aldehyde to form a 2-*H*-4-benzylidene imidazolone followed by Pd-catalyzed C–H arylation with an aryl iodide.[10] Singh also reported the synthesis of imidazolinones from L-phenylalanine in two steps, through reacting L-phenylalanine with chloroacetyl chloride under Schotten–Baumann coupling conditions followed by a PCl_3-mediated cyclization.[11] Nevertheless, Zaitseva prepared arylidene-1-*H*-imidazol-5-(4*H*)-ones by reacting an azidoacetic acid amide with PPh_3 to obtain a phosphazene, which was then treated with an aliphatic anhydride followed by condensation with an aldehyde.[12] Despite being elegant synthetic methods, they suffer from the drawbacks of a multistep synthesis, poor yields, limited substrate scope and the necessity to prepare pre-functionalized starting materials. Since benzylidene imidazolones, as the chromophores of GFPs, have acquired prominent importance in molecular biology and biochemistry, a method to provide imidazolones in a convenient, efficient and atom-economical way is necessary.

Recently, ultrasound irradiation has emerged as a green and clean technique for organic synthesis. The breakdown of cavitation bubbles in a liquid generates hot spots with a short lifetime and high pressure. This phenomenon creates turbulence in the system and reduces the reaction time and side products, and improves the reaction yield.[13] Herein, we report a serendipitous strategy discovered for the synthesis of substituted 4-arylidene imidazolin-5-ones *via* a multi-component reaction between amino acid esters, isothio(seleno)cyanates and α-bromoketones. The isolation of an intermediate (**8a**)

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†Electronic supplementary information (ESI) available: Full spectroscopic data (^1H and ^{13}C NMR, HRMS, HPLC and IR) of compounds **9a–9j**, **5a–5q** and **7a–7l**. CCDC 1884822 for **7a** and 1882293 for **9h**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ob03111h

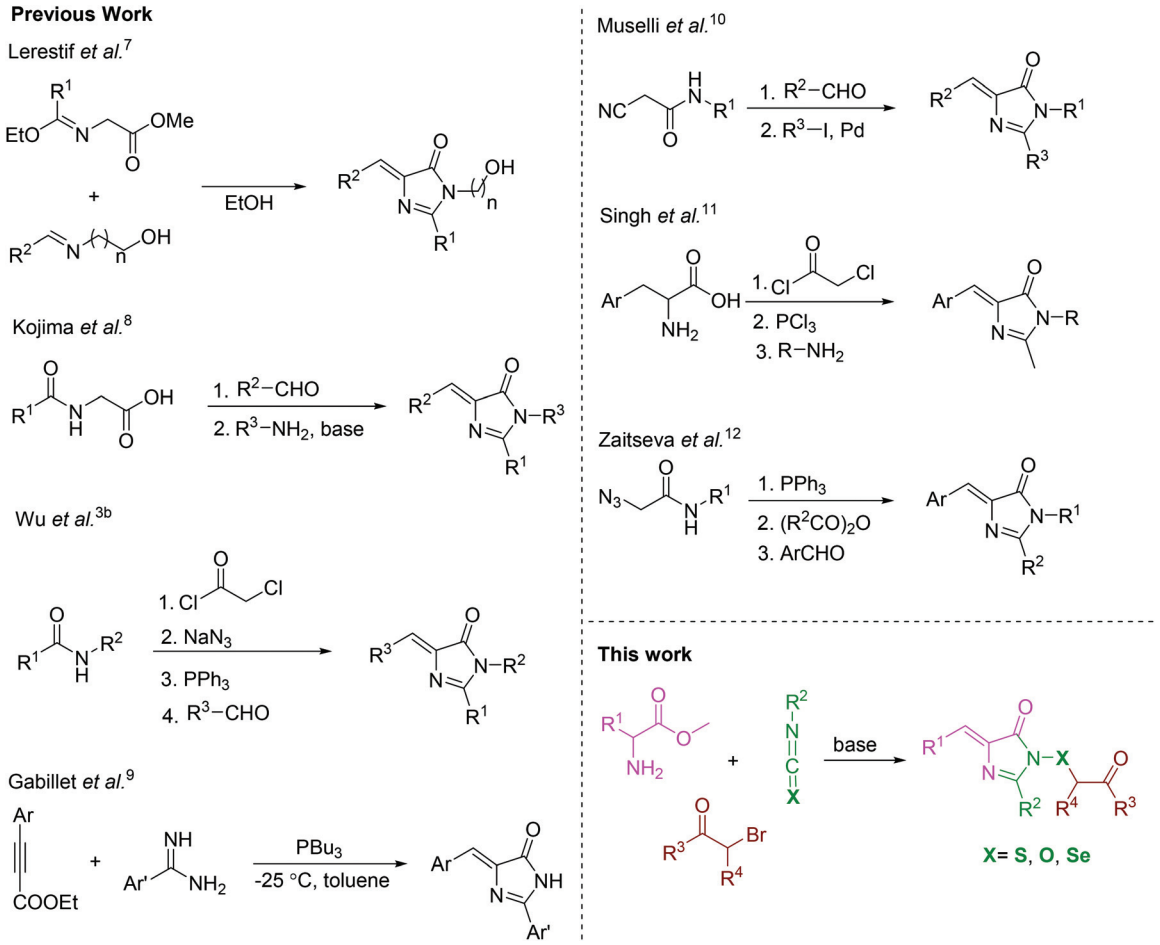


Fig. 1 Various methods for the synthesis of *N*-substituted 4-arylidene imidazolin-5-ones.

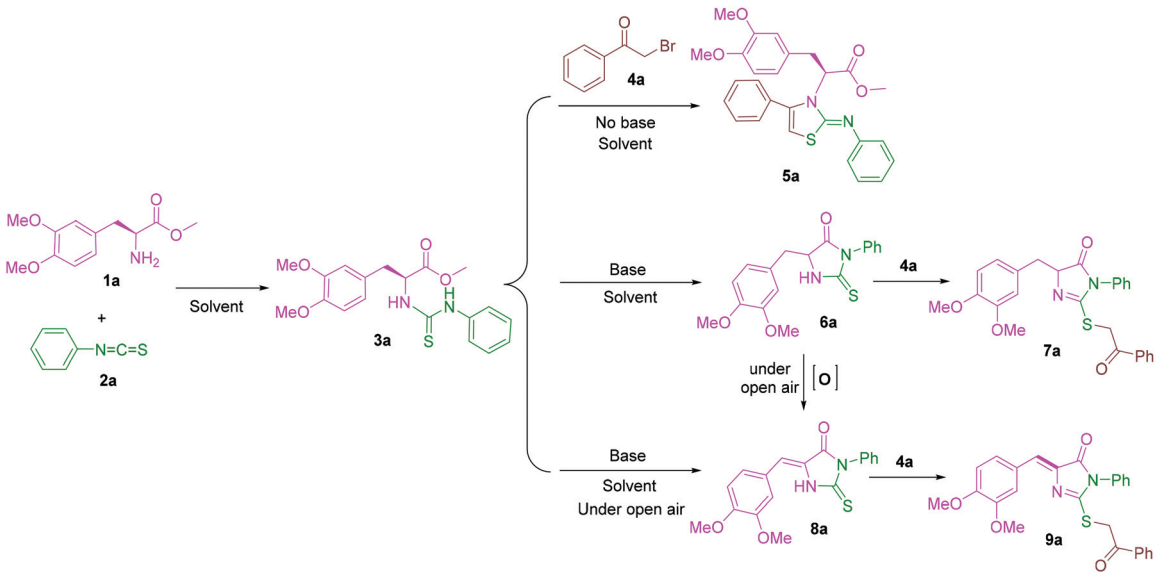
provided evidence for the course of the reaction mechanism. In addition, the strategy can be expanded to synthesize 2-iminothia(seleno)(oxo)zolines and 2-thioxoimidazolin-4-ones.

Results and discussion

Our investigation commenced with reaction of L-3,4-dimethoxyphenylalanine methyl ester **1a** with phenyl isothiocyanate **2a** and 2-bromoacetophenone **4a** in CH_3CN at room temperature for 2 hours, and 2-iminothiazole **5a** along with an unreacted intermediate thiourea **3a** were obtained in 65% and 18% yields, respectively (Table 1, entry 1). Elevation of the reaction temperature to 50 °C and conducting the reaction for 1 hour, increased the reaction yield to 80% (Table 1, entry 2). When the same reaction was carried out under sonication at 50 °C, **5a** was obtained in 90% yield after 30 minutes (Table 1, entry 3).

In an attempt to examine the effect of a base on the reaction, various organic and inorganic bases were screened. Surprisingly, use of 1 equivalent of $NaHCO_3$ in the same coupling reaction at room temperature afforded 2-thioxoimidazolin-4-one **7a** (41%) and a thiohydantoin intermediate **6a** (35%) (Table 1, entry 4). Upon subjecting the reaction to sonication at 50 °C, **7a** was obtained in 85% yield after 3 hours (Table 1, entry 5). Lower yields were observed when the reaction was performed at 50 °C over 4 h or under reflux conditions (Table 1, entries 6–7). During the screening of organic bases such as DIPEA and Et_3N, we found that using one equivalent of base afforded **7a** in moderate to good yields, while the use of 3 equivalents of Et_3N over 3 hours yielded a new product **9a** in 89% yield under open-air conditions (Table 1, entries 8–10). Use of triethylamine under conventional heating conditions for 0.5 h afforded **7a** in 82% yield (Table 1, entry 11). We found that the solvent had a significant effect on the reaction pathway. Use of a protic solvent, such as methanol, afforded a carbamate as well as a β-ketoamine in preference to the desired product[14,15] (Table 1, entry 12). Dichloromethane required a longer reaction time (16 h) to provide **7a** in 80% yield, and with 1,4-dioxane the same product was obtained in 75% yield after 24 h (Table 1, entries 13–14). To investigate the formation of **9a**, two additional reactions were performed under argon and an open air atmosphere. Formation of the product **9a** was observed only under open-air conditions, indicating that generation of the double bond was caused by air oxidation.

Table 1 Optimization of the reaction conditions[a]



					Yield[b] (%)					
Entry	Base	Solvent	Temp (°C)	Time (h)	**3a**	**6a**	**8a**	**5a**	**7a**	**9a**
1	—	CH_3CN	rt	2	18	—	—	65	—	—
2	—	CH_3CN	50	1	—	—	—	80	—	—
3	—	CH_3CN	50[c]	0.5	—	—	—	90	—	—
4	$NaHCO_3$	CH_3CN	rt	24	—	35	—	—	41	—
5	$NaHCO_3$	CH_3CN	50[c]	3	—	—	—	—	85	—
6	$NaHCO_3$	CH_3CN	50	4	—	—	—	—	81	—
7	$NaHCO_3$	CH_3CN	reflux	2	—	—	—	—	78	—
8	DIPEA	CH_3CN	rt	4	—	—	—	—	62	—
9	Et_3N	CH_3CN	rt	1	—	—	—	—	79	—
10	Et_3N[d]	CH_3CN	50	3	—	—	—	—	—	89
11	Et_3N	CH_3CN	50	0.5	—	—	—	—	82	—
12	$NaHCO_3$	CH_3OH	50	2	—	—	—	—	—	—
13	$NaHCO_3$	CH_2Cl_2	50	16	—	—	—	—	80	—
14	$NaHCO_3$	1,4-dioxane	50	24	—	—	—	—	75	—

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.5 mmol), **4a** (1.5 mmol), base (1 mmol), solvent (5 mL). [b] Isolated yield. [c] Reaction was sonicated. [d] Et_3N (3 eq.) was used.

The structures of compounds **5a** and **7a** were first established using spectroscopic analysis. The proton NMR spectrum of **5a** exhibited a signal at 5.53 ppm due to the C–H of the thiazole ring as well as a peak at 95 ppm in the carbon NMR spectrum. The disappearance of the singlet peak from the methyl ester and appearance of diastereotopic doublets at 4.48, 3.26 and 3.08 ppm were observed from the proton NMR of **7a**. Single X-ray crystal analysis of **7a** revealed that the five-membered oxoimidazolin-4-one ring is in a twisted form and overall the structure is non-planar (Fig. 2).

Chiral HPLC analysis of **5a** indicated that a single isomer (98% ee) was obtained under the optimized reaction conditions, which was further confirmed through preparation of **5a′** from D-dopa. Conversely, racemization was observed in the case of **7a**.

After establishing the optimized conditions, the substrate scope of this strategy was also investigated (Table 2).

Bromoacetophenones bearing electron-withdrawing as well as electron-donating substituents provided the desired products **9b**, **9c** and **9d** in good yields. Notably, sterically bulky α-bromoacetophenones (R^4 = $-CH_3$, –Ph) successfully participated in the reaction to furnish **9f**, **9g** and **9i** in good yields. The use of aliphatic or aromatic isothio(seleno)cyanates had no effect on the yields of **9**. The group R^1 had a moderate effect on the reaction yields and the products **9c**, **9d** and **9j** were obtained in relatively lower yields. The absolute structure of **9h** containing a selenium atom was determined using X-ray analysis (Fig. 3).

In an extension of the present strategy, two different types of heterocycles were explored through altering the reaction conditions (Tables 3 and 4). 2-Iminothiazolines **5** were formed when the reaction was carried out without a base, while 2-thioxoimidazolin-4-ones **7** were obtained when the same coupling reaction was performed with a base. Various iso-

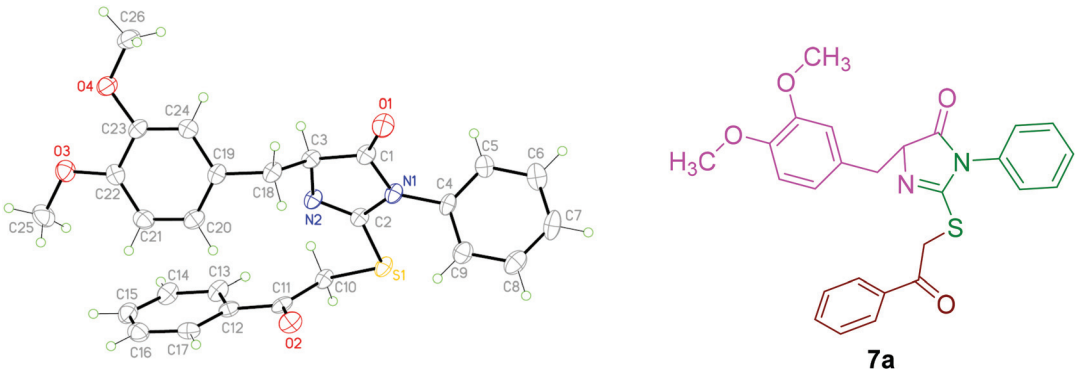
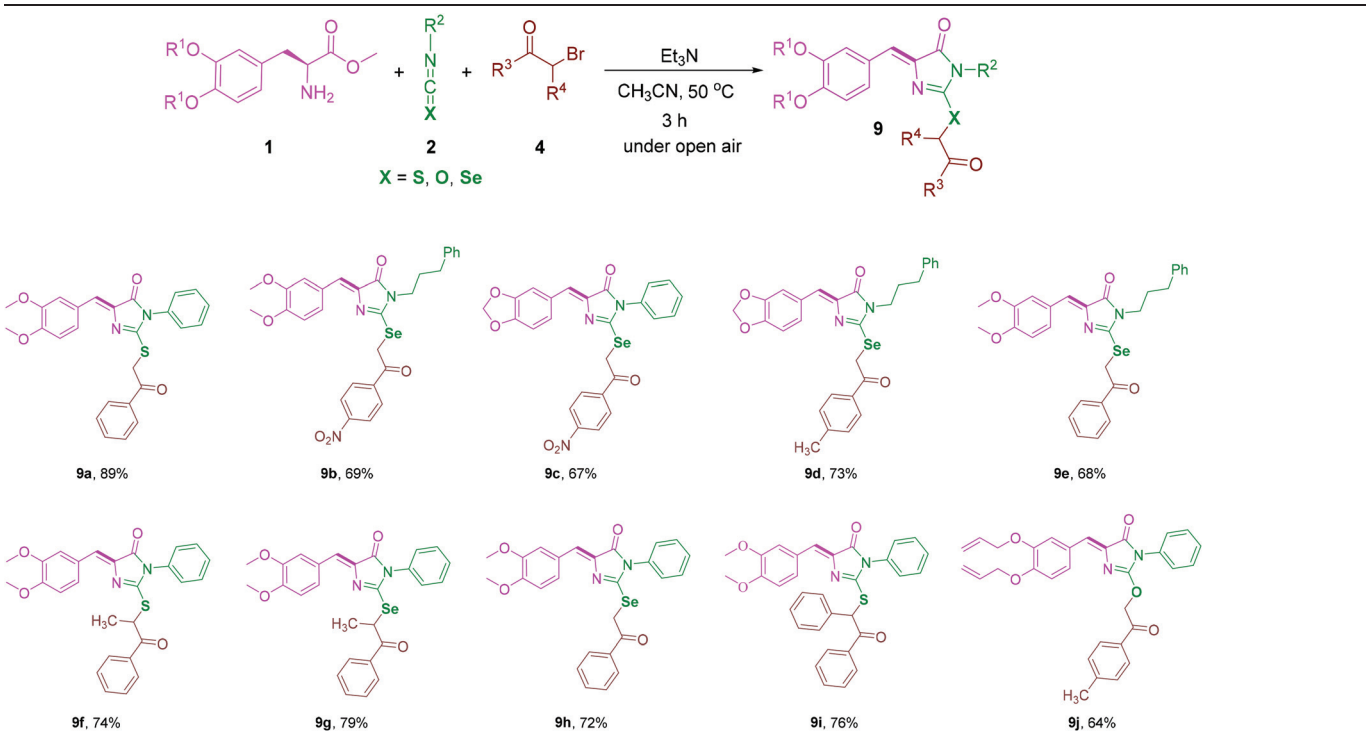


Fig. 2 ORTEP diagram of **7a**.

Table 2 Substrate scope investigation for 4-arylidene imidazolin-5-ones **9** [a]



[a] Reaction conditions: **1** (1 mmol), **2** (1.5 mmol), **4** (1.5 mmol), Et_3N (3 equiv.) and CH_3CN (5 mL).

cyanates and α-bromoacetophenones afforded the desired compounds **5** and **7** in good yields. Decreases in the yields were observed with aliphatic isothio-, seleno-, and iso-cyanates compared to aromatic isothiocyanates. The reactions of α-bromoacetophenones bearing electron-withdrawing, electron-donating and halogen substituents on the benzene ring occurred smoothly to provide the corresponding products in moderate to good yields. Moreover, a secondary α-bromoacetophenone (R^4 = $-CH_3$) also provided the product **7i** in good yield. It is notable that an aliphatic isocyanate failed to react in the presence of $NaHCO_3$ and a stronger base (NaH) was required to furnish the desired products **5o** and **7k**, albeit in 68% and 48% yields, respectively. The lower yield of **7k** was attributed to formation of 1,3-dicyclohexylurea, *via* cyclodimerization of the isocyanates, as a side product in 25% yield.[16]

Based on the isolation of intermediates **3** and **6**, literature reports and the obtained results, a possible mechanism for the synthesis of compounds **9**, **5** and **7** was proposed and is depicted in Scheme 1. The reaction proceeds through formation of urea **3** from L-amino acid methyl ester **1** and isocyanate **2**. A base-mediated cyclization of **3** would afford thiohydantoin intermediate **6**, which then either tautomerizes to

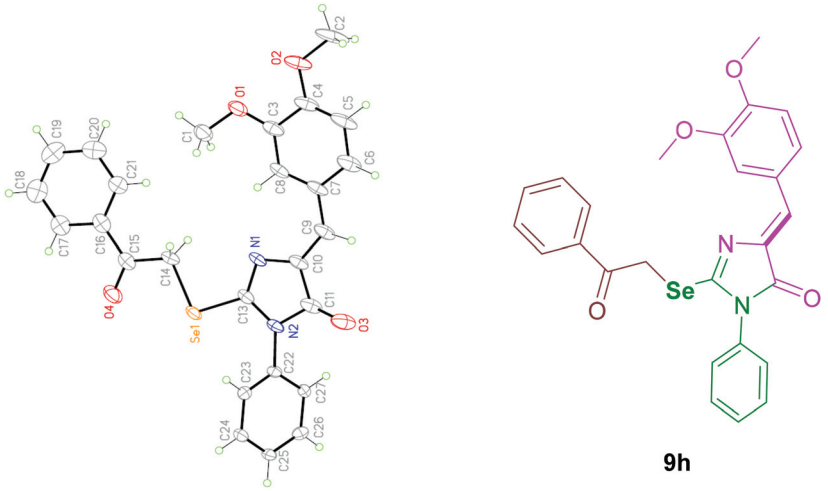
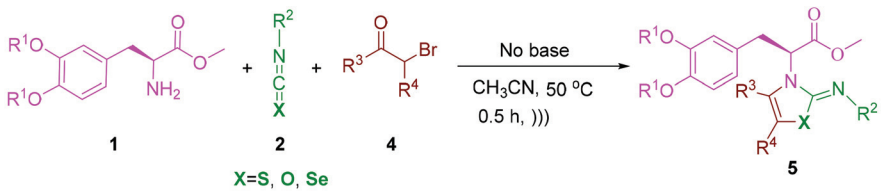
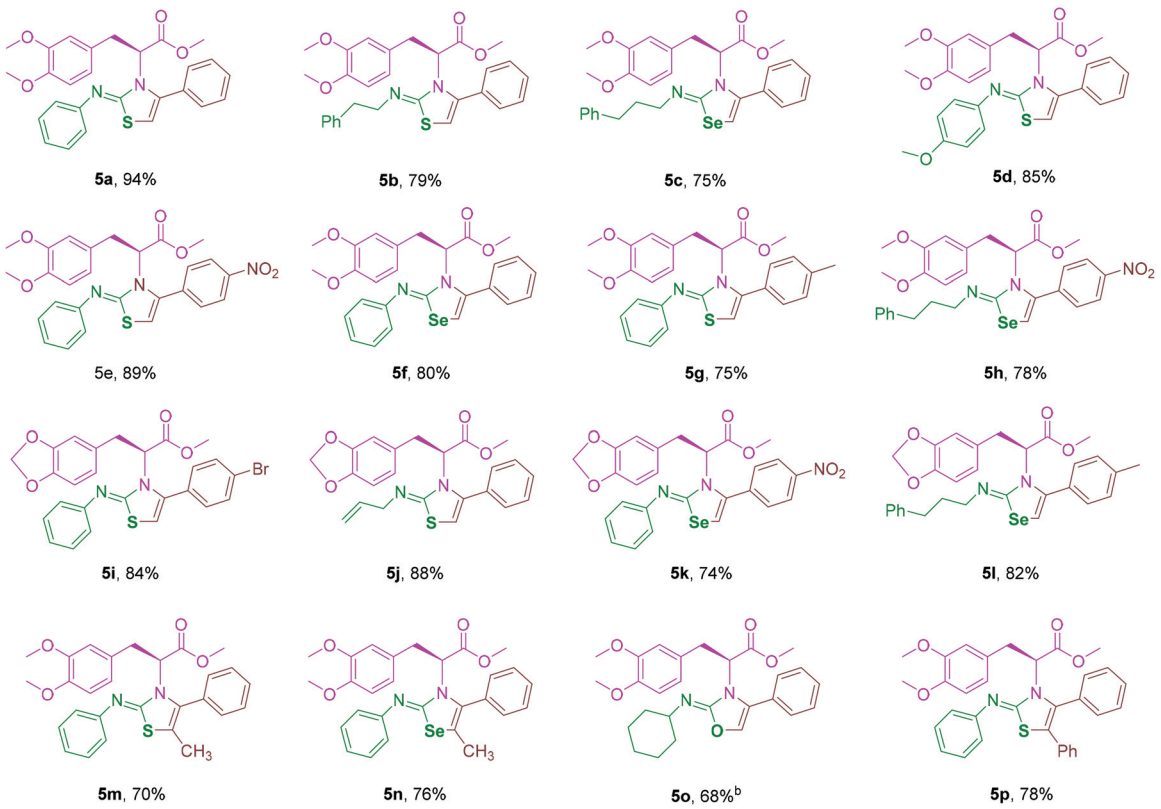


Fig. 3 ORTEP diagram of **9a**.

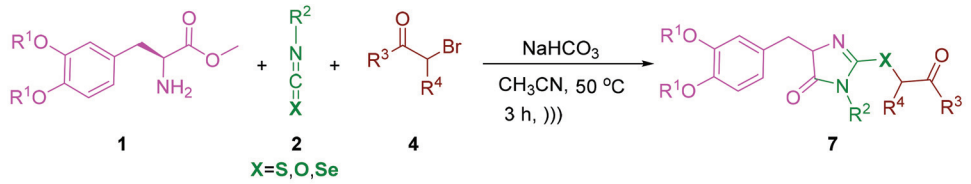
Table 3 Substrate scope investigation for 2-iminothiazolines **5** [a]

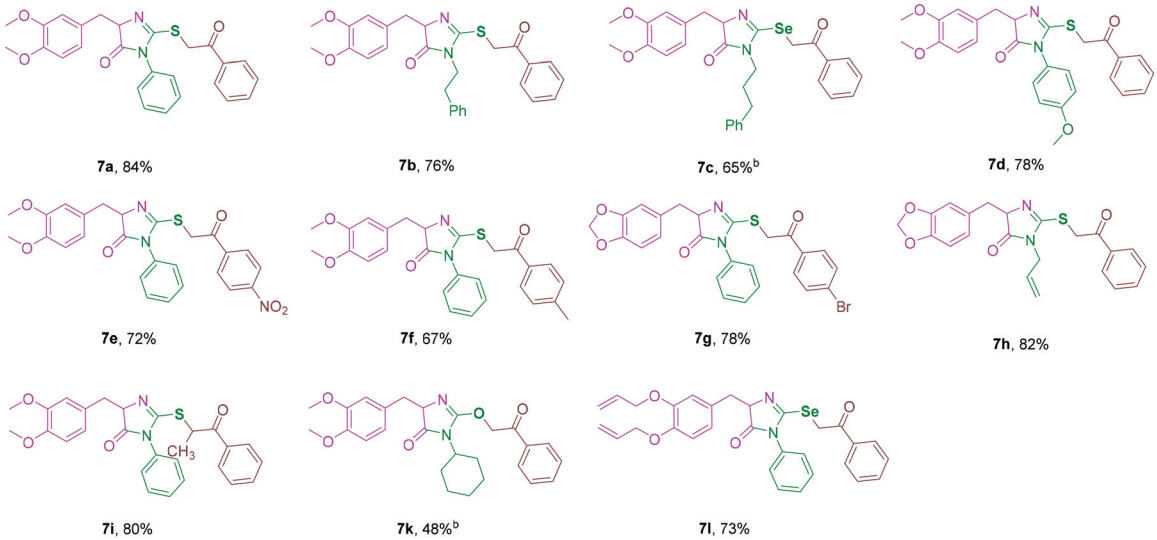




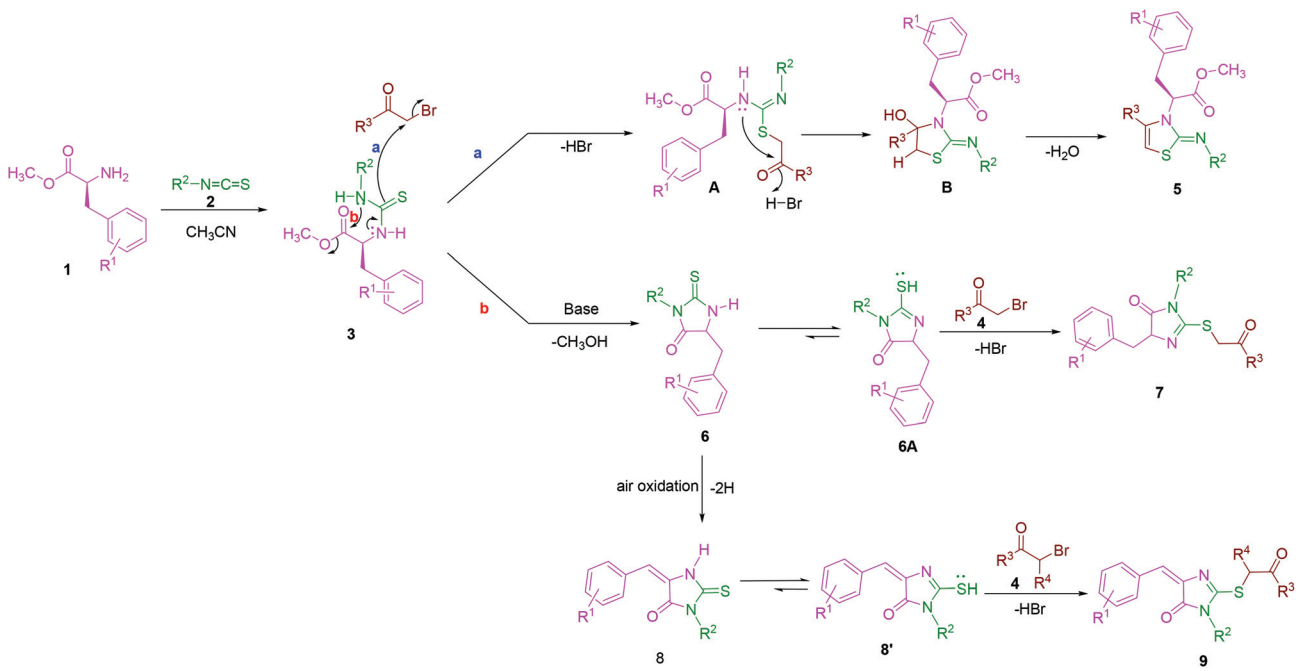
[a] Reaction conditions: **1** (1 mmol), **2** (1.5 mmol), **4** (1.5 mmol) and CH_3CN (5 mL). [b] 1 equiv. of NaH was used.

Table 4 Substrate scope investigation for 2-thioxoimidazolin-4-ones **7** [a]





[a] Reaction conditions: **1** (1 mmol), **2** (1.5 mmol), **4** (1.5 mmol), $NaHCO_3$ (1 equiv.) and CH_3CN (5 mL). [b] 3 equiv. of NaH was used. 1,3-dicyclohexylurea (25%) was isolated.



Scheme 1 A possible mechanism for the synthesis of 4-arylidene imidazolin-5-one **9**, 2-iminothiazoline **5** and 2-thioxoimidazolin-4-one **7**.

form **6A**, and its subsequent alkylation affords 2-thioxoimidazolin-4-one **7** through path **b**, or undergoes air oxidation to afford 5-benzylidene 2-thioxoimidazolidin-4-one **8**. **8** may consequently undergo tautomerization to form 5-benzylidene-2-mercapto-4*H*-imidazol-4-one **8′**, followed by alkylation with α-bromoketone **4** to provide substituted 4-arylidene imidazolin-5-one **9**. In path **a**, nucleophilic addition of thiourea **3** to α-bromoketone **4** would yield isothiourea **A**. Then, intramolecular addition followed by elimination of a water molecule would provide 2-iminothiazoline **5**.

Conclusions

We have developed a simple one-pot synthesis of 4-arylidene imidazolin-5-ones *via* a multicomponent reaction of L-amino acid methyl esters, iso-, isothio- or isoseleno-cyanates, and α-bromoketones. The isolation of hydantoin and 2-thioxoimidazolidin-4-one intermediates indicated that the reaction sequence proceeds through formation of a hydantoin first followed by subsequent air oxidation. Use of the mild base $NaHCO_3$ afforded 2-thioxoimidazolin-4-ones, whereas using 3 equivalents of triethylamine provided 4-arylidene imidazolin-5-ones. Extension of this methodology was demonstrated through synthesizing 2-iminothiazolines and 2-thioxoimidazolin-4-ones, either under neutral or basic reaction conditions.

General methods

^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded using a 400-MR automated spectrometer. Chemical shifts are reported in parts per million (ppm) on the δ scale relative to an internal standard (TMS). Analytical thin-layer chromatography (TLC) was performed using 0.25 mm silica gel-coated Kiselgel 60 F_{254} plates. The ultrasound-assisted reactions were carried out in a Elmasonic P ultrasonic cleaner with a frequency of 37 kHz. Flash chromatography was performed using the indicated solvent and silica gel 60 (Merck, 230–400 mesh). High-resolution mass spectrometry (HRMS) spectra were recorded in ESI mode using a TOF mass spectrometer. Enantiomeric excess (ee) values were determined using chiral HPLC with a Lux 5μm cellulose-1 (250 × 4.6 mm) analytical column. Melting points were recorded with Yanaco micro-melting point apparatus and are uncorrected. All materials were purchased from commercial sources and used without further purification.

Experimental section

Representative procedure for the synthesis of (*Z*)-5-(3,4-dimethoxybenzylidene)-2-((2-oxo-2-phenylethyl)thio)-3-phenyl-3,5-dihydro-4*H*-imidazol-4-one (9a)

To a stirred solution of phenyl isothiocyanate **2a** (85 mg, 0.62 mmol) in acetonitrile (10 mL) was added triethylamine (1.74 mL, 3 mmol) and methyl (*S*)-2-amino-3-(3,4-dimethoxyphenyl)propanoate **1a** (100 mg, 0.41 mmol), and the reaction mixture was sonicated at 50 °C for 3 h. To the above reaction mixture, 2-bromoacetophenone **4a** (125 mg, 0.62 mmol) was added and the reaction was further sonicated for 2 h. After completion of the reaction, the solvent was evaporated. The residue was diluted with water (15 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified using flash column chromatography (8–15% ethyl acetate in hexanes) to afford (*S*)-4-(3,4-dimethoxybenzyl)-2-((2-oxo-2-phenylethyl)thio)-1-phenyl-1*H*-imidazol-5(4*H*)-one **9a** as a pale yellow solid (160 mg, 84%).

Yellow solid, (82%, 157 mg); mp: 80–82 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (d, J = 7.2 Hz, 2H), 7.92 (s, 1H), 7.74 (t, J = 7.4 Hz, 1H), 7.62–7.57 (m, 3H), 7.55–7.53 (m, 1H), 7.47–7.42 (m, 3H), 6.89 (s, 1H), 6.65 (d, J = 8.5 Hz, 2H), 5.09 (s, 2H), 3.74 (s, 3H), 3.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 168.5, 159.2, 151.2, 148.9, 136.5, 134.3, 133.8, 132.6, 129.6, 129.3, 128.9, 128.6, 127.4, 127.0, 126.9, 125.9, 113.6, 110.9, 55.9, 55.6, 42.4, 19.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}N_2O_4S$: 459.1379, found: 459.1377; IR (cm^{-1}, neat): 3059, 2919, 2851, 1420.

Representative procedure for the synthesis of (*S*,*Z*)-methyl 3-(3,4-dimethoxy-phenyl)-2-(4-phenyl-2-(phenylimino)thiazol-3(2*H*)-yl)propanoate (5a)

To a stirred solution of phenyl isothiocyanate **2a** (85 mg, 0.62 mmol) in acetonitrile (10 mL), methyl (*S*)-2-amino-3-(3,4-dimethoxy-phenyl)propanoate **1a** (100 mg, 0.41 mmol) was added dropwise and the reaction mixture was sonicated at 50 °C for 30 min. 2-Bromoacetophenone **4a** (125 mg, 0.62 mmol) was added to the above reaction mixture and the reaction was further sonicated for 30 min. After completion of the reaction, the solvent was removed. The residue was diluted with water (15 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was purified using flash column chromatography (2–5% ethyl acetate in hexanes) to afford (*S*,*Z*)-methyl 3-(3,4-dimethoxyphenyl)-2-(4-phenyl-2-(phenylimino)thiazol-3(2*H*)-yl)propanoate **5a** as a yellow oil (186 mg, 94%).

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 3H), 7.25 (m, 2H), 7.11 (m, 2H), 7.06 (m, 1H), 6.76 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 8.1 Hz, 1H), 6.47 (dd, J = 8.1, 2.0 Hz, 1H), 6.36 (d, J = 2.0 Hz, 1H), 5.53 (s, 1H), 4.54 (dd, J = 11.1, 4.0 Hz, 1H), 3.94 (m, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.67 (s, 3H), 3.16 (dd, J = 14.0, 4.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 148.8, 147.7, 140.3, 131.0, 130.0, 129.3, 129.0, 128.3, 123.0, 121.3, 112.1, 111.2, 95.1, 60.2, 56.0, 55.5, 52.6, 32.4, 31.8, 14.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{27}N_2O_4S$: 475.1692, found: 475.1692; $[\alpha]_D^{27}$ = −115.08 (c = 0.0429, CH_2Cl_2); HPLC analysis: 10% i-PrOH/hexane, 0.3 mL min^{-1}, 254 nm; 99% ee; t_R = 8.9 min.

Representative procedure for the synthesis of 5-benzyl-2-((2-oxo-2-phenylethyl)thio)-3-phenyl-3,5-dihydro-4*H*-imidazol-4-one (7a)

To a stirred solution of phenyl isothiocyanate **2a** (85 mg, 0.62 mmol) in acetonitrile (10 mL) was added $NaHCO_3$ (105 mg, 1.25 mmol) and methyl (*S*)-2-amino-3-(3,4-dimethoxyphenyl)propanoate **1a** (100 mg, 0.41 mmol), and the reaction mixture was sonicated at 50 °C for 2 h. To the above reaction mixture, 2-bromoacetophenone **4a** (125 mg, 0.62 mmol) was added and the reaction was further sonicated for 1.5 h. After completion of the reaction, the solvent was evaporated. The residue was diluted with water (15 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified using flash column chromatography (8–15% ethyl acetate in hexanes) to afford (*S*)-4-(3,4-dimethoxybenzyl)-2-((2-oxo-2-phenylethyl)thio)-1-phenyl-1*H*-imidazol-5(4*H*)-one **7a** as a pale yellow solid (161 mg, 84%).

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.4, 1.2 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 7.52–7.38 (m, 3H), 6.97–6.94 (m, 2H), 6.76 (s, 1H), 6.71 (s, 2H), 4.67 (d, J = 2.0 Hz, 2H), 4.48 (dd, J = 6.2, 4.3 Hz, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 3.26 (dd, J = 13.8, 4.3 Hz, 1H), 3.08 (dd, J = 13.8, 6.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 180.2, 161.0, 148.4, 147.9, 135.5, 133.9, 131.8, 129.5, 129.3, 128.8, 128.5, 128.3, 127.3, 122.0, 112.9, 110.8, 69.9, 55.9, 55.8, 38.7, 37.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}N_2O_4S$: 461.1535, found: 461.1530.

Conflicts of interest

There are no conflicts to declare.

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