Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 5032

www.rsc.org/obc

COMMUNICATION

# $FeCl_3$ promoted highly regioselective [3 + 2] cycloaddition of dimethyl 2-vinyl and aryl cyclopropane-1,1-dicarboxylates with aryl isothiocyanates†

**Huina Wang,[a] Wei Yang,[a] Hong Liu,[a] Wei Wang*[a,b] and Hao Li*[a,b]**

***Received 6th April 2012, Accepted 21st May 2012***
**DOI: 10.1039/c2ob25682g**



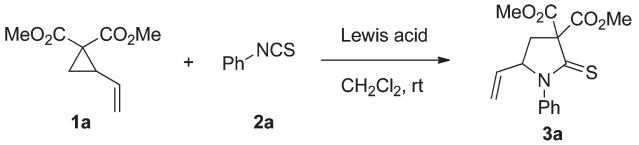
**A $FeCl_3$ promoted [3 + 2] annulation of dimethyl 2-vinyl and arylcyclopropane-1,1-dicarboxylate with aryl isothiocyanates has been developed to give pyrrolidine-2-thiones in good yields with high regioselectivity.**

## Introduction

Lewis acid promoted [3 + 2] annulation reactions of functionalized cyclopropanes have received considerable attention in the past decade.[1] The processes serve as a powerful tool for the facile construction of synthetically valuable 5-membered rings such as cyclopentanes, tetrahydrofurans, pyrrolidines and pyrrolidin-2-ones from respective olefins,[2] carbonyls,[3] imines[4] and isocyanates[5] as dipolarophiles. In these transformations, it is recognized that transition metals such as palladium,[6] rhodium,[7] ruthenium,[8] nickel,[9] and non-toxic ytterbium[10] are often employed as effective promoters. Recently the use of less toxic and inexpensive Lewis acids such as Mg(II),[4d,11] Cu(II),[12] and Fe (III)[13] for the related processes has gained significant interest. Nevertheless, such cases are still very rare.

Pyrrolidine-2-thiones can be used as intermediates to synthesize biologically important compounds, displaying intriguing anti-cancer properties.[14] However, methods for the synthesis of pyrrolidine-2-thiones from isothiocyanates are very rare. Kim reported samarium diiodide promoted intramolecular cyclization of β-ketoisothiocyanates.[15] Wang reported the Michael/cyclization of α-isothiocyanato imides, esters, and lactones with methyleneindolinones.[16] Herein, we describe our results on investigating a new [3 + 2] cycloaddition of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate with commercially available and inexpensive isocyanates to afford pyrrolidine-2-thiones in the presence of $FeCl_3$. To the best of our knowledge, although reactions of 2-vinylcyclopropane-1,1-dicarboxylates with isocyanates[5] and the only one cycloaddition example of special 2,2-dimethoxy-cyclopropane-1-carboxylates with phenyl isothiocyanate[17] have been reported, the study represents the preparation of pyrrolidine-2-thiones using the powerful [3 + 2] cycloaddition approach from cyclopropanes and isothiocyanates promoted by $FeCl_3$.

**Table 1** Lewis acids screening for [3 + 2] cycloaddition reactions




1a 2a 3a

| Entry[a] | Lewis acid | Additive | Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | $FeCl_3$ | — | 24 | 45 |
| 2[c] | $FeCl_3$ | 4 Å MS | 24 | 65 |
| 3[c] | $Pd(OAc)_2$ | 4 Å MS | 48 | 0 |
| 4[c] | AgOTf | 4 Å MS | 48 | 0 |
| 5[c] | $CuCl_2$ | 4 Å MS | 48 | 0 |
| 6[c] | $Zn(NTf_2)_2$ | 4 Å MS | 48 | 0 |
| 7[c] | $Yb(OTf)_3$ | 4 Å MS | 48 | 0 |
| 8[c] | $Sc(OTf)_3$ | 4 Å MS | 24 | Trace |
| 9[c] | $AlCl_3$ | 4 Å MS | 24 | 17 |
| 10[c] | $In(OTf)_3$ | 4 Å MS | 24 | 54 |
| 11[c] | $Sn(OTf)_2$ | 4 Å MS | 24 | 49 |

[a] On a 0.3 mmol scale, 1.0 eq. of Lewis acid. [b] Isolated yield. [c] 250 mg of 4 Å MS was added in the reaction mixture.

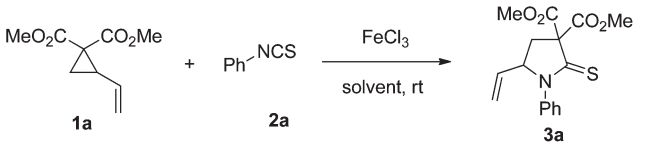
## Results and discussion

We began our initial [3 + 2] cycloaddition study using dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**1a**) (0.3 mmol) and isothiocyanatobenzene (**2a**) (1.2 eq.) as reactants in the present of $FeCl_3$ (1.0 eq.) as the Lewis acid in $CH_2Cl_2$ at rt (Table 1). To our delight, the reaction occurred to give the expected cycloaddition product pyrrolidine-2-thione (**3a**) in low yield (45%) after stirring for 24 h (entry 1). Our continuing investigations showed that the addition of 4 Å molecular sieves (MS) could improve the reaction yield to 65% under the same reaction conditions (entry 2). Then we examined various Lewis acids including $Pd(OAc)_2$, AgOTf, $CuCl_2$, $Zn(NTf_2)_2$, $Yb(OTf)_3$, $Sc(OTf)_3$,

[a]*Shanghai Institute of Materia Medica, Shanghai, 201203, P. R. China. E-mail: weiwangsimm@gmail.com; Fax: (+86) 21-6425-3739*
[b]*School of Pharmacy, East China University of Science and Technology, 130 Meilong Lu, Shanghai, 200237, P. R. China. E-mail: hli77@ecust.edu.cn; Fax: (+86) 21-6425-3299*

†Electronic supplementary information (ESI) available: Experimental procedures, compound characterizations, and $^1H$ and $^{13}C$ NMR spectra. See DOI: 10.1039/c2ob25682g

**Table 2** Solvent effect for [3 + 2] cycloaddition reactions




| Entry[a] | Lewis acid | Solvent | Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | $FeCl_3$ (1 eq.) | $CH_2Cl_2$ | 24 | 65 |
| 2 | $FeCl_3$ (1 eq.) | $CHCl_3$ | 24 | 34 |
| 3 | $FeCl_3$ (1 eq.) | $ClCH_2CH_2Cl$ | 24 | 67 |
| 4 | $FeCl_3$ (1 eq.) | $CH_3CN$ | 48 | 16 |
| 5 | $FeCl_3$ (1 eq.) | Toluene | 48 | <10 |
| 6 | $FeCl_3$ (1 eq.) | Benzene | 48 | <10 |
| 7 | $FeCl_3$ (0.3 eq.) | $ClCH_2CH_2Cl$ | 36 | 56 |

[a] On a 0.3 mmol scale. [b] Isolated yield.

$In(OTf)_3$ and $Sn(OTf)_2$ for this [3 + 2] cycloaddition process. However, it was found that they were inferior to $FeCl_3$ promoted annulation reaction (entries 3–11).

The above results indicated that $FeCl_3$ had the highest activity for this cycloaddition reaction. The study of solvent effect was next investigated under optimized conditions (Table 2). The reaction in chloroform ran much slower than that in dichloromethane, and the isolated yield was only about half of that in $CH_2Cl_2$ (entries 1–2). The reactions in $ClCH_2CH_2Cl$ had a little higher yield than that in dichloromethane (entry 3, 67%). Nevertheless, $CH_3CN$, toluene and benzene gave rise to even poorer yields and all the isolated yields were less than 20% after 48 h (entries 4–6). Notably, reducing the amount of $FeCl_3$ (0.3 eq., entry 7) could still catalyze the [3 + 2] cycloaddition reaction, although the progress was much slower and reaction yield was decreased (56%, entry 7).

With the optimized reaction conditions in hand, structurally diverse cyclopropanes and isothiocyanates were investigated to prove the generality of the reaction. The results were summarized in Fig. 1. Notably, in all cases, the processes proceeded highly regioselectively. Exploration of the structural demand of dipolarophiles revealed that significant structure variation could be tolerated. It appeared that the electronic and steric effects were limited. The arylisothiocyanates bearing electron-withdrawing groups of Br, Cl at *para*-, *meta*- and *ortho*-position with steric hindrance (Fig. 1, **3b–3e**, **3i**, **3k**, and **3m**), and -donating groups of methyl and methoxy group (**3f–3g**, **3j** and **3l**) and neutral Ph groups (**3h**) gave 53–68% yields of cycloaddition products. When benzyl isothiocyanate reacted with **1a**, the reaction was sluggish and the reaction yield was only 28% after 48 h (**3n**). A structural variation of 1,3-dipole components was also examined. Vinyl (**3a–g**) and aryl (**3h–m**) cyclopropanes could participate in the reactions. However, the limitation of the process was also recognized. When dimethyl 2-benzylcyclopropane-1,1-dicarboxylate was used, no cycloaddition product was found even after 48 h.

A plausible reaction mechanism was proposed, as depicted in Scheme 1. Lewis acid activates the oxygen of the ester to open the cyclopropane to generate 1,3-dipoles **A** and **B**. It is hypothesized that the conjugated π system of vinyl or phenyl ring can

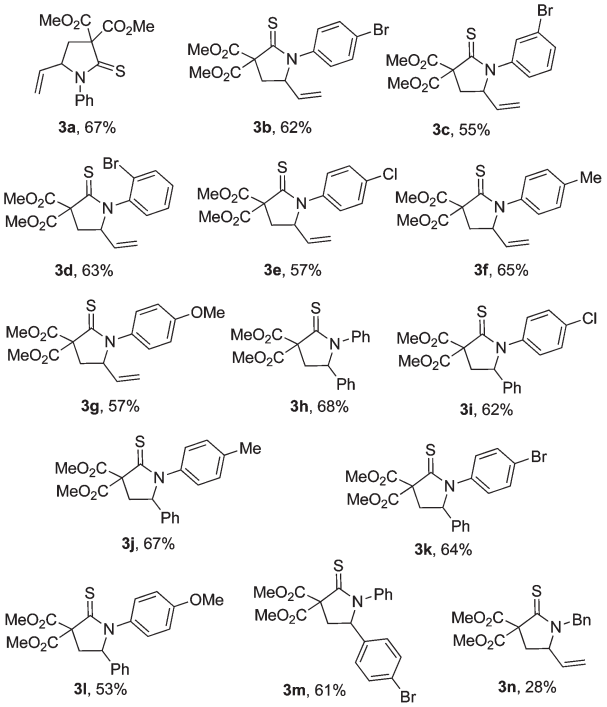
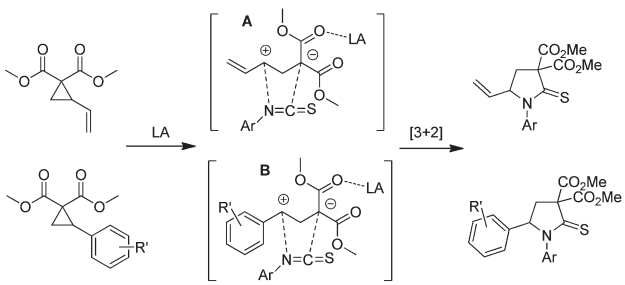



**Fig. 1** Scopes of pyrrolidine-2-thiones.




**Scheme 1** Proposed mechanism for the [3 + 2] cycloaddition reactions.

stabilize the positive charge of 1,3-dipoles to help the subsequent [3 + 2] annulation. Alkylcyclopropane won't stabilize the positive charge to make the reaction happen due to the absence of the conjugated π system. The germinal diester group dictates the observed regioselectivity of the products formed.

## Conclusion

In conclusion, we have developed an unprecedented $FeCl_3$ promoted [3 + 2] cycloaddition between functionalized cyclopropanes and isothiocyanates with a relatively broad substrate scope. Notably, the process takes place in a highly regioselective manner to give structurally diverse pyrrolidine-2-thiones, which are difficult to obtain through classic methods. Further exploration of the chemistry and the biologically interesting pyrrolidine-2-thiones are being pursued in our laboratory.

## Experimental

### General information

Unless stated otherwise, the reagents and solvents of the highest purity available were used as purchased or purified/dried by standard procedures when necessary. $^1$H and $^{13}$C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for $^1$H NMR are recorded as follows: chemical shift ($\delta$, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for $^{13}$C NMR are reported in terms of chemical shift ($\delta$, ppm).

### General procedure for synthesis of pyrrolidine-2-thiones

All reactions were carried out under a nitrogen atmosphere. $FeCl_3$ (49 mg, 0.3 mmol), 4 Å MS (250 mg), cyclopropane (0.3 mmol in 1.5 mL of $CH_2Cl_2$) and imine (0.36 mmol in 1.5 mL of $CH_2Cl_2$) was sequentially added to an oven-dried reaction tube. The resulting solution was further stirred at room temperature. After the reaction was complete (monitored by TLC), the mixture was filtered rapidly through a glass funnel with a thin layer of silica gel, washed with $CH_2Cl_2$. The filtrate was concentrated and the residue was purified by flash column chromatography (petroleum ether– EtOAc = 15 : 1) to afford the desired product.

**Dimethyl 1-phenyl-2-thioxo-5-vinylpyrrolidine-3,3-dicarboxylate (3a).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.37–7.28 (m, 2H), 7.17–7.09 (m, 1H), 6.97 (m, 2H), 5.75 (ddd, $J$ = 16.9, 10.0, 8.4 Hz, 1H), 5.35–5.21 (d, $J$ = 16.9 Hz, 1H), 5.14 (d, $J$ = 10.0 Hz, 1H), 4.20 (ddd, $J$ = 10.5, 8.4, 5.2 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.01 (dd, $J$ = 13.1, 5.2 Hz, 1H), 2.68 (dd, $J$ = 13.1, 10.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 168.02, 167.81, 167.78, 150.87, 135.48, 128.90, 125.04, 119.91, 118.57, 70.63, 53.74, 53.56, 50.07, 41.46. HRMS (ESI) cacld for $[M + Na]^+$ $C_{16}H_{17}NO_4SNa$: 342.0776, found: 342.0777.

**Dimethyl 1-(4-bromophenyl)-2-thioxo-5-vinylpyrrolidine-3,3-dicarboxylate (3b).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.49–7.39 (m, 2H), 6.89–6.81 (m, 2H), 5.74 (ddd, $J$ = 16.9, 10.0, 8.4 Hz, 1H), 5.31–5.25 (m, 1H), 5.22–5.07 (m, 1H), 4.29–4.13 (m, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.01 (dd, $J$ = 13.1, 5.2 Hz, 1H), 2.68 (dd, $J$ = 13.1, 10.5 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 168.85, 167.78, 167.57, 149.76, 135.22, 131.98, 121.77, 118.79, 118.14, 70.69, 53.77, 53.59, 50.26, 41.46. HRMS (ESI) cacld for $[M + H]^+$ $C_{16}H_{17}NO_4SBr$: 398.0062, found: 398.0081.

**Dimethyl 1-(3-bromophenyl)-2-thioxo-5-vinylpyrrolidine-3,3-dicarboxylate (3c).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.25 (d, $J$ = 7.3 Hz, 1H), 7.19 (t, $J$ = 7.9 Hz, 1H), 7.13 (s, 1H), 6.90 (d, $J$ = 7.8 Hz, 1H), 5.75 (dt, $J$ = 18.2, 9.1 Hz, 1H), 5.29 (d, $J$ = 16.9 Hz, 1H), 5.16 (d, $J$ = 10.0 Hz, 1H), 4.22 (td, $J$ = 10.1, 5.4 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 3.01 (dd, $J$ = 13.1, 5.2 Hz, 1H), 2.69 (dd, $J$ = 13.0, 10.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 169.44, 167.71, 167.49, 152.01, 135.14, 130.26, 127.82, 122.93, 122.40, 118.79, 118.55, 70.65, 53.74, 53.55, 50.30, 41.50. HRMS (ESI) cacld for $[M + Na]^+$ $C_{16}H_{16}BrNO_4S$: 419.9881, found: 419.9865.

**Dimethyl 1-(2-bromophenyl)-2-thioxo-5-vinylpyrrolidine-3,3-dicarboxylate (3d).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.56 (dd, $J$ = 7.9, 1.0 Hz, 1H), 7.26 (ddd, $J$ = 7.7, 6.8, 1.2 Hz, 1H), 7.05–6.92 (m, 2H), 5.76 (ddd, $J$ = 16.9, 9.9, 8.5 Hz, 1H), 5.29 (d, $J$ = 16.9 Hz, 1H), 5.15 (d, $J$ = 10.0 Hz, 1H), 4.34–4.20 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.04 (dd, $J$ = 13.1, 5.2 Hz, 1H), 2.73 (dd, $J$ = 13.1, 10.5 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 170.05, 167.68, 167.50, 149.11, 135.23, 132.97, 127.96, 126.15, 120.23, 118.80, 115.00, 70.49, 53.68, 53.55, 50.52, 41.72. HRMS (ESI) cacld for $[M + H]^+$ $C_{16}H_{17}NO_4SBr$: 398.0062, found: 398.0074.

**Dimethyl 1-(4-chlorophenyl)-2-thioxo-5-vinylpyrrolidine-3,3-dicarboxylate (3e).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39–7.19 (m, 2H), 7.01–6.83 (m, 2H), 5.74 (ddd, $J$ = 16.9, 9.9, 8.4 Hz, 1H), 5.28 (d, $J$ = 16.8 Hz, 1H), 5.15 (d, $J$ = 10.0 Hz, 1H), 4.21 (ddd, $J$ = 10.4, 8.4, 5.2 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.01 (dd, $J$ = 13.1, 5.2 Hz, 1H), 2.68 (dd, $J$ = 13.1, 10.5 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 168.85, 167.82, 167.61, 149.26, 135.24, 130.33, 129.03, 121.42, 118.79, 70.70, 53.77, 53.59, 50.26, 41.45. HRMS (ESI) cacld for $[M + Na]^+$ $C_{16}H_{16}NO_4SClNa$: 376.0386, found: 376.0407.

**Dimethyl 2-thioxo-1-(*p*-tolyl)-5-vinylpyrrolidine-3,3-dicarboxylate (3f).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.22–7.05 (m, 2H), 6.95–6.83 (m, 2H), 5.75 (ddd, $J$ = 16.9, 10.0, 8.4 Hz, 1H), 5.27 (d, $J$ = 16.8 Hz, 1H), 5.13 (d, $J$ = 10.0 Hz, 1H), 4.20 (ddd, $J$ = 10.5, 8.4, 5.3 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.00 (dd, $J$ = 13.1, 5.2 Hz, 1H), 2.66 (dd, $J$ = 13.1, 10.6 Hz, 1H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz): $\delta$ 168.10, 167.85, 167.12, 148.30, 135.58, 134.69, 129.45, 119.95, 118.48, 70.65, 53.72, 53.54, 50.02, 41.34, 20.98. HRMS (ESI) cacld for $[M + H]^+$ $C_{17}H_{20}NO_4S$: 334.1113, found 334.1110.

**Dimethyl 1-(4-methoxyphenyl)-2-thioxo-5-vinylpyrrolidine-3,3-dicarboxylate (3g).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.04–6.94 (m, 2H), 6.92–6.83 (m, 2H), 5.75 (ddd, $J$ = 16.9, 9.9, 8.4 Hz, 1H), 5.28 (d, $J$ = 16.9 Hz, 1H), 5.14 (d, $J$ = 10.0 Hz, 1H), 4.21 (ddd, $J$ = 10.5, 8.5, 5.3 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.79 (s, 3H), 2.99 (dd, $J$ = 13.1, 5.3 Hz, 1H), 2.64 (dd, $J$ = 13.1, 10.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 168.16, 167.89, 166.35, 157.12, 143.77, 135.62, 121.69, 118.49, 113.99, 70.80, 55.35, 53.72, 53.53, 50.10, 41.13. HRMS (ESI) cacld for $[M + H]^+$ $C_{17}H_{20}NO_5S$: 350.1062, found: 350.1047.

**Dimethyl 1,5-diphenyl-2-thioxopyrrolidine-3,3-dicarboxylate (3h).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41–7.37 (m, 2H), 7.37–7.27(m, 5H), 7.16–7.09 (m, 1H), 7.05–6.99 (m, 2H), 4.74 (dd, $J$ = 11.7, 4.9 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.17 (dd, $J$ = 13.1, 5.0 Hz, 1H), 2.98 (dd, $J$ = 13.1, 11.7 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 168.13, 167.75, 167.68, 150.85, 137.68, 128.93, 128.79, 128.36, 127.64, 125.09, 120.03, 71.20, 53.84, 53.60, 51.03, 43.68. HRMS (ESI) cacld for $[M + H]^+$ $C_{20}H_{20}NO_4S$: 370.1113, found: 370.1103.

**Dimethyl 1-(4-chlorophenyl)-5-phenyl-2-thioxopyrrolidine-3,3-dicarboxylate (3i).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40–7.36 (m, 2H), 7.36–7.28 (m, 5H), 7.04–6.89 (m, 2H), 4.76 (dd, $J$ = 11.6, 4.9 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.18 (dd, $J$ = 13.1,

5.0 Hz, 1H), 2.98 (dd, $J$ = 13.1, 11.7 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 168.70, 167.94, 167.58, 149.26, 137.44, 130.40, 129.07, 128.84, 128.46, 127.61, 121.54, 71.27, 53.88, 53.64, 51.24, 43.69. HRMS (ESI) cacld for $[M + H]^+$ $C_{20}H_{18}ClNO_4S$: 404.0723, found: 404.0719.

**Dimethyl 5-phenyl-2-thioxo-1-(*p*-tolyl)pyrrolidine-3,3-dicarboxylate (3j).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.59 (d, $J$ = 7.7 Hz, 2H), 7.50 (dt, $J$ = 19.0, 7.1 Hz, 3H), 7.35 (d, $J$ = 7.8 Hz, 2H), 7.15 (d, $J$ = 7.7 Hz, 2H), 4.96 (dd, $J$ = 11.6, 4.8 Hz, 1H), 4.15 (s, 3H), 4.07 (s, 3H), 3.38 (dd, $J$ = 13.1, 4.9 Hz, 1H), 3.17 (t, $J$ = 12.3 Hz, 1H), 2.52 (s, 3H). $^{13}$C NMR (100 MHz): $\delta$ 168.10, 167.71, 166.86, 148.20, 137.72, 134.65, 129.40, 128.68, 128.23, 127.56, 120.00, 71.15, 53.71, 53.46, 50.89, 43.49, 20.90. HRMS (ESI) cacld for $[M + Na]^+$ $C_{21}H_{21}NO_4NaS$: 406.1089, found: 406.1082.

**Dimethyl 1-(4-bromophenyl)-5-phenyl-2-thioxopyrrolidine-3,3-dicarboxylate (3k).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52–7.42 (m, 2H), 7.41–7.20 (m, 5H), 6.97–6.86 (m, 2H), 4.76 (dd, $J$ = 11.6, 4.9 Hz, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.18 (dd, $J$ = 13.1, 5.0 Hz, 1H), 2.98 (dd, $J$ = 13.1, 11.7 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 168.72, 167.88, 167.53, 149.73, 137.38, 132.00, 128.82, 128.44, 127.58, 121.88, 118.19, 71.24, 53.86, 53.62, 51.23, 43.68. HRMS (ESI) cacld for $[M + H]^+$ $C_{20}H_{19}NO_4SBr$: 448.0218, found: 448.0225.

**Dimethyl 1-(4-methoxyphenyl)-5-phenyl-2-thioxopyrrolidine-3,3-dicarboxylate (3l).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39 (dd, $J$ = 8.1, 1.4 Hz, 2H), 7.42–7.36 (m, 3H), 7.05–6.99 (m, 2H), 6.90–6.83 (m, 2H), 4.75 (dd, $J$ = 11.7, 4.9 Hz, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 3.79 (s, 3H), 3.16 (dd, $J$ = 13.1, 5.0 Hz, 1H), 2.94 (dd, $J$ = 13.0, 11.8 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 168.27, 167.85, 166.15, 157.16, 143.73, 137.83, 128.78, 128.32, 127.67, 121.83, 114.02, 71.37, 55.37, 53.81, 53.56, 51.05, 43.39. HRMS (ESI) cacld for $[M + Na]^+$ $C_{21}H_{21}NO_5SNa$: 422.1038, found: 422.1028.

**Dimethyl 5-(4-bromophenyl)-1-phenyl-2-thioxopyrrolidine-3,3-dicarboxylate (3m).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44 (d, $J$ = 8.2 Hz, 2H), 7.34 (t, $J$ = 7.8 Hz, 2H), 7.29–7.21 (m, 2H), 7.13 (t, $J$ = 7.4 Hz, 1H), 7.02 (dd, $J$ = 8.3, 0.9 Hz, 2H), 4.70 (dd, $J$ = 11.6, 4.9 Hz, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 3.16 (dd, $J$ = 13.1, 5.0 Hz, 1H), 2.91 (dd, $J$ = 13.0, 11.7 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ 167.90, 167.53, 167.00, 150.68, 136.81, 131.88, 129.29, 128.93, 125.17, 122.18, 119.93, 71.04, 53.82, 53.59, 50.30, 43.55. HRMS (ESI) cacld for $[M + Na]^+$ $C_{20}H_{18}NO_4NaSBr$: 470.0038, found: 470.0046.

**Dimethyl 1-benzyl-2-thioxo-5-vinylpyrrolidine-3,3-dicarboxylate (3n).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.73–7.04 (m, 5H), 5.81 (ddd, $J$ = 16.9, 9.9, 8.4 Hz, 1H), 5.32 (d, $J$ = 16.9 Hz, 1H), 5.18 (d, $J$ = 10.0 Hz, 1H), 4.53 (s, 2H), 4.23 (ddd, $J$ = 10.6, 8.4, 5.2 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.98 (dd, $J$ = 13.0, 5.2 Hz, 1H), 2.64 (dd, $J$ = 13.0, 10.6 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ 168.31, 168.11, 166.36, 138.69, 135.83, 128.23, 127.43, 126.71, 118.57, 70.53, 60.73, 53.60, 53.42, 50.06, 41.93. HRMS (ESI) cacld for $[M + H]^+$ $C_{17}H_{20}NO_4S$: 334.1113, found: 334.1106.

## Acknowledgements

The financial support from the Shanghai Pujiang Program (11PJ1411900), East China University of Science & Technology and the China 111 Project (Grant B07023) is appreciated.

## Notes and references

1 For reviews on annulation of cyclopropanes, see: (*a*) H.-U. Reissig and R. Zimmer, *Chem. Rev.*, 2003, **103**, 1151; (*b*) M. Rubin, M. Rubina and V. Gevorgyan, *Chem. Rev.*, 2007, **107**, 3117; (*c*) T. F. Schneider and D. B. Werz, *Org. Lett.*, 2011, **13**, 1848.
2 Selected examples: (*a*) M. Komatsu, I. Suehiro, Y. Horiguchi and I. Kuwajima, *Synlett*, 1991, 771; (*b*) W. F. Berkowitz and S. C. Grenetz, *J. Org. Chem.*, 1976, **41**, 10; (*c*) B. Bajtos, M. Yu, H. Zhao and B. L. Pagenkopf, *J. Am. Chem. Soc.*, 2007, **129**, 9631; (*d*) K. Sapeta and M. A. Kerr, *Org. Lett.*, 2009, **11**, 2081.
3 Perspective article: (*a*) M. J. Campbell, J. S. Johnson, A. T. Parsons, P. D. Pohlhaus and S. D. Sanders, *J. Org. Chem.*, 2010, **75**, 6317. Pioneering examples: (*b*) H.-U. Reissig, *Tetrahedron Lett.*, 1981, **22**, 2981; (*c*) S. Shimada, Y. Hashimoto, A. Sudo, M. Hasegawa and K. Saigo, *J. Org. Chem.*, 1992, **57**, 7126; (*d*) S. Shimada, Y. Hashimoto, T. Nagashima, M. Hasegawa and K. Saigo, *Tetrahedron*, 1993, **49**, 1589; (*e*) S. Shimada, Y. Hashimoto and K. Saigo, *J. Org. Chem.*, 1993, **58**, 5226; (*f*) Y. Sugita, K. Kawai and I. Yokoe, *Heterocycles*, 2000, **53**, 657; (*g*) Y. Sugita, K. Kawai and I. Yokoe, *Heterocycles*, 2001, **55**, 135; (*h*) Z. Han, S. Uehira, T. Tsuritani, H. Shinokubo and K. Oshima, *Tetrahedron*, 2001, **57**, 987.
4 Selected examples: (*a*) P. B. Alper, C. Meyers, A. Lerchner, D. R. Siegel and E. M. Carreira, *Angew. Chem., Int. Ed.*, 1999, **38**, 3186; (*b*) C. A. Carson and M. A. Kerr, *J. Org. Chem.*, 2005, **70**, 8242; (*c*) Y.-B. Kang, Y. Tang and X.-L. Sun, *Org. Biomol. Chem.*, 2006, **4**, 299; (*d*) A. T. Parsons, A. G. Smith, A. J. Neel and J. S. Johnson, *J. Am. Chem. Soc.*, 2010, **132**, 9688.
5 K. Yamamoto, T. Ishida and J. Tsuji, *Chem. Lett.*, 1987, 1157.
6 (*a*) T. Nishimura and S. Uemura, *J. Am. Chem. Soc.*, 2000, **122**, 12049–12050; (*b*) S. Matsumura, Y. Maeda, T. Nishimura and S. Uemura, *J. Am. Chem. Soc.*, 2003, **125**, 8862.
7 (*a*) M. Gozin, A. Weisman, Y. Ben-David and D. Milstein, *Nature*, 1993, **364**, 699; (*b*) M. Murakami, K. Takahashi, H. Amii and Y. Ito, *J. Am. Chem. Soc.*, 1997, **119**, 9307; (*c*) S. C. Bart and P. J. Chirik, *J. Am. Chem. Soc.*, 2003, **125**, 886; (*d*) P. A. Wender, N. M. Deschamps and R. Sun, *Angew. Chem., Int. Ed.*, 2006, **45**, 3957; (*e*) T. Nishimura, T. Katoh, K. Takatsu, R. Shintani and T. Hayashi, *J. Am. Chem. Soc.*, 2007, **129**, 14158; (*f*) A. M. Dreis and C. J. Douglas, *J. Am. Chem. Soc.*, 2008, **131**, 412; (*g*) T. Seiser and N. Cramer, *Angew. Chem., Int. Ed.*, 2008, **47**, 9294; (*h*) T. Seiser and N. Cramer, *J. Am. Chem. Soc.*, 2010, **132**, 5340.
8 (*a*) T. Kondo, K. Kodoi, E. Nishinaga, T. Okada, Y. Morisaki, Y. Watanabe and T. Mitsudo, *J. Am. Chem. Soc.*, 1998, **120**, 5587; (*b*) T. Shimada and Y. Yamamoto, *J. Am. Chem. Soc.*, 2003, **125**, 6646.
9 (*a*) M. Murakami, S. Ashida and T. Matsuda, *J. Am. Chem. Soc.*, 2005, **127**, 6932; (*b*) Y. Nakao, T. Yukawa, Y. Hirata, S. Oda, J. Satoh and T. Hiyama, *J. Am. Chem. Soc.*, 2006, **128**, 7116; (*c*) M. P. Watson and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2008, **130**, 12594.
10 (*a*) D. B. England, T. D. O. Kuss, R. G. Keddy and M. A. Kerr, *J. Org. Chem.*, 2001, **66**, 4704; (*b*) O. A. Ivanova, E. M. Budynina, A. O. Chagarovskiy, A. E. Kaplun, I. V. Trushkov and M. Y. Melnikova, *Adv. Synth. Catal.*, 2011, **353**, 1125.
11 (*a*) A. Lerchner and E. M. Carreira, *J. Am. Chem. Soc.*, 2002, **124**, 14826; (*b*) C. Meyers and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2003, **42**, 694.
12 J. Qu, C. Deng, J. Zhou, X. Sun and Y. Tang, *J. Org. Chem.*, 2009, **74**, 7684.
13 During our study on this research, the following ion catalytic reactions were reported recently: (*a*) F. Benfatti, F. Nanteuil and J. Waser, *Org. Lett.*, 2012, **14**, 386; (*b*) A. Dieskau, M. Holzwarth and B. Plietker, *J. Am. Chem. Soc.*, 2012, **134**, 5048, DOI: 10.1021/ja300294a.
14 P. Magnus, J. Mendoza, A. Stamford, M. Ladlow and P. Willis, *J. Am. Chem. Soc.*, 1992, **114**, 10232.
15 M. S. Cho, I. S. Lee, S. H. Kang and Y. H. Kim, *Chem.–Eur. J.*, 2005, **11**, 1452.
16 Y. Cao, X. Jiang, L. Liu, F. Shen, F. Zhang and R. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 9124.
17 M. L. Graziano and G. Cimminiello, *J. Chem. Res. (S)*, 1989, **2**, 42.