Convenient Structural Diversity-Guided Synthesis of Functionalized Sulfur-Containing Heterocycles *via* α-Substituted Cyanoacetamides

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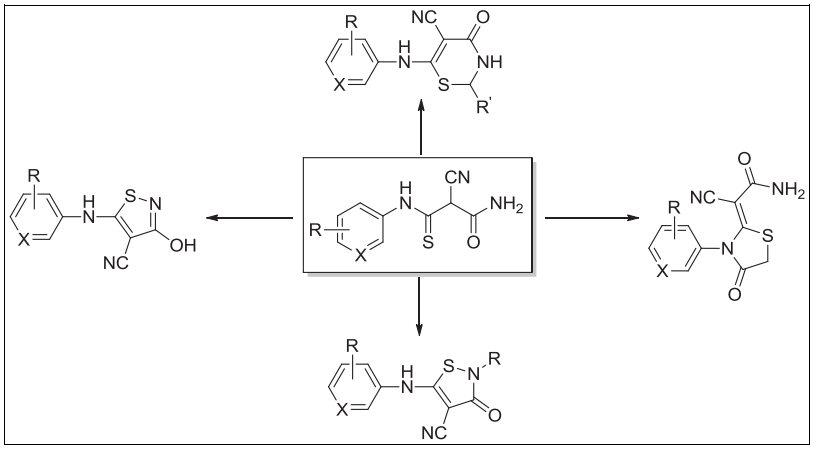
Received July 4, 2016
DOI 10.1002/jhet.2792
Published online 00 Month 2016 in Wiley Online Library (wileyonlinelibrary.com).



A convenient molecular diversity-oriented synthesis of various functional sulfur-containing heterocyclic scaffolds mainly including isothiazole, 2*H*-1,3-thiazine, and thiazolidine via different methods from α-substituted cyanoacetamides is described. The target molecules have been identified on the basis of analytical spectral data, which may serve as useful structural subunits in the fields of drug discovery.

J. Heterocyclic Chem., **00,** 00 (2016).

INTRODUCTION

Sulfur is an essential element in the fields of life science and organic chemistry [1]. Many sulfur-containing building blocks play an important role in modern organic synthesis and are also widely used in the pharmaceutical industry, agrochemical chemistry, and materials science [2–6]. Especially, many sulfur heterocyclic compounds have been developed as drugs (such as penicillin [7], sulfasomizole [8], saccharin [9], enzalutamide [10]; Fig. 1) and agrochemicals (such as penthiopyrad [11], isotianil [12], tiadinil [13], thiamethoxam [14], and fluensulfone [15]; Fig. 1). In addition, some sulfur-containing heterocycles and their derivatives can also be used as important synthons for further transformation to related heterocycles via diverse reaction conditions [16–19].

Up to now, organosulfur compounds have received considerable attention because of their wide area of application, so the development of novel functionalized multi-substituted sulfur-containing heterocycles as potential pharmaceuticals is still an important area of interest in life science and the search for an efficient method for the preparation of these heterocyclic derivatives under mild conditions is not only highly desirable but also necessary. In this short communication, we would like to present a convenient structural diversity-oriented procedure for access to various functional sulfur-containing heterocycles that exploit mild ring-closure methods and easily available raw materials (Fig. 2), and these heterocycles might serve as useful structural subunits in the fields of drug discovery.

RESULTS AND DISCUSSION

Considering the convenient synthesis to construct the structure diversity of sulfur-containing heterocyclic derivatives, four different types of compounds (**5**, **6**, **7**, and **8**) were investigated and obtained via α-substituted cyanoacetamides **4**. The general synthetic route for the target compounds is outlined in Scheme 1.

For the sake of structural diversity, we attempted the preparation of four different types of heterocyclic compounds (**5**, **6**, **7**, and **8**) using the key intermediates α-substituted cyanoacetamides **4** as described in Scheme 1. In order to explore these transformations, the convenient preparation of intermediate heteroaryl-isothiocyanates **3** is obviously important. Although the substituted isothiocyanate can be prepared by several methods [20–25], we desire to develop convenient and effective methods for these heterocyclic isothiocyanates. The representative compound 6-chloropyridin-3-amine

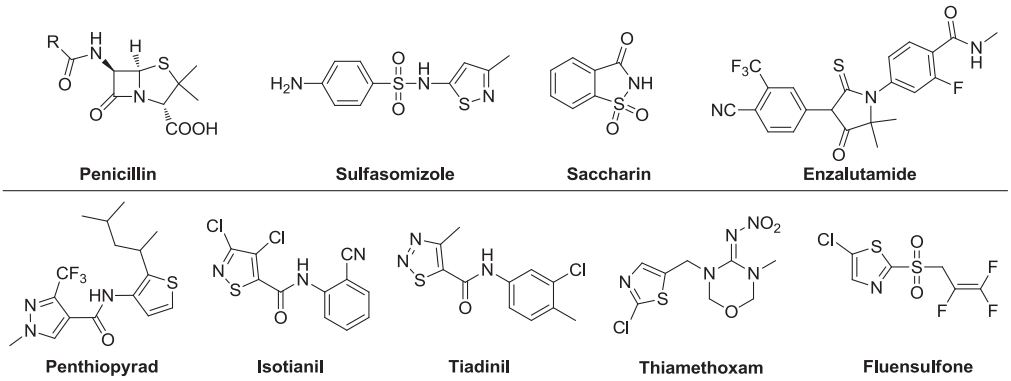


Figure 1. Representative structures of sulfur-containing heterocycles.

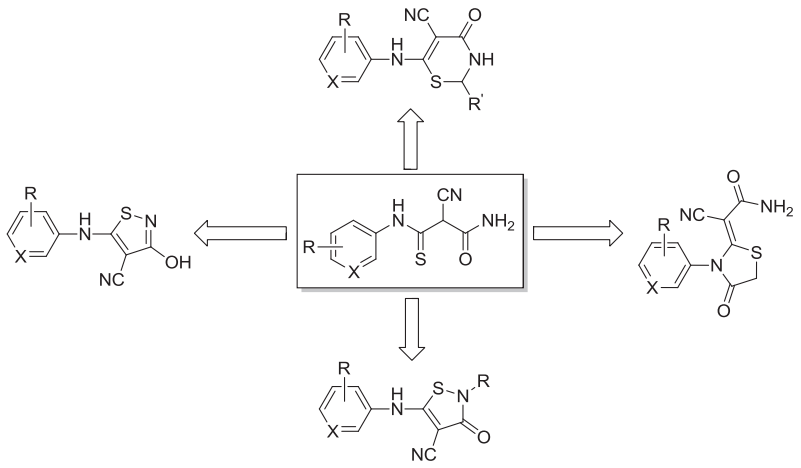
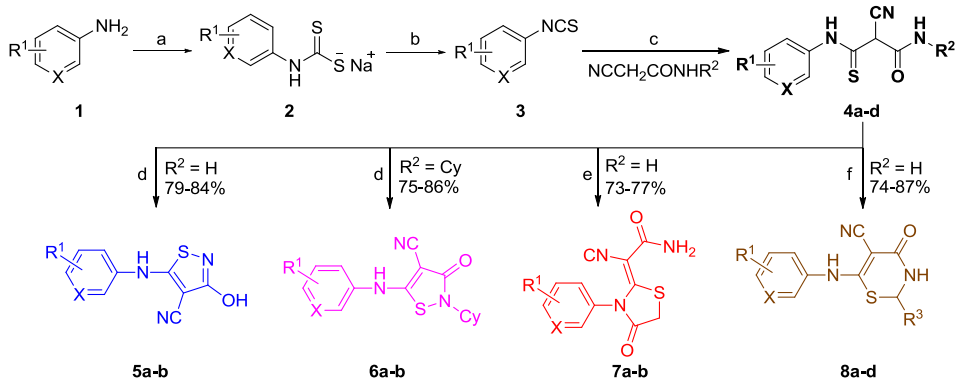


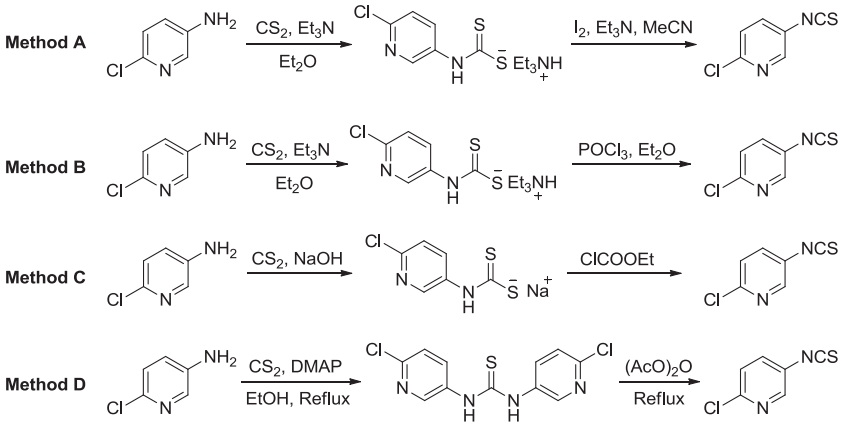
Figure 2. Construction strategy for various functional heterocycles.

Scheme 1. Synthetic route for sulfur-containing heterocyclic derivatives via α-substituted cyanoacetamides. Reagents and conditions: a. CS_2, NaOH; b. ClCOOEt; c. KOH, DMA; d. Br_2, CH_3COOEt; e. $BrCH_2COOEt$, DMF; f. R^3CHO, Cat. *p*-$MeC_6H_4SO_3H$, EtOH. [Color figure can be viewed at wileyonlinelibrary.com]



was chosen as a substrate for the optimization of the reaction conditions, and four different methods have been fully investigated (Scheme 2). The screened results indicated that method C gives the best conversion and yields (78%); however, the target intermediate can also be obtained via methods A and B with very low yields (34% and 28%, respectively). Especially, for Method B, the reaction is very intense when the phosphorus oxychloride is dropped, and this reaction is difficult to handle. Furthermore, the transformation cannot be completed according to method D, which just stay at the stage of intermediate 1,3-bis(6-chloropyridin-3-yl)thiourea.

Scheme 2. The optimization of the reaction conditions for heterocyclic isothiocyanate.



After the optimization of the conditions for intermediates **3**, various transformations for different heterocyclic derivatives have been fully explored. The key intermediates α-substituted cyanoacetamides **4** were conveniently obtained via nucleophilic additional reaction between compounds **3** and substituted cyanoacetamide under the optimized alkaline conditions. In the process of screening for the practical reaction conditions, the different reaction systems mainly including Et_3N/MeCN, Et_3N/DMF, and Et_3N/DMA were tried, but did not work for this procedure. Then, the strong inorganic base in polar solvent was adopted to explore this transformation, and the results demonstrated that this system can conveniently prepare the target compounds under simple process.

Subsequently, the constructions of different sulfur heterocyclic derivatives was explored via different heterocyclization reactions. First, the intermediate **4** was transformed into the corresponding substituted isothiazole derivatives **5** via bromine oxidation reaction. However, the separation and purification of the products were obviously affected by different solvents. When we adopted dichloromethane as solvent in this heterocyclization reaction, the target compounds was not easy to separate from the mixtures, but in the ethyl acetate, it was easy to separate the products because of the differences in the solubility of the raw materials and products. Then, the substituted isothiazole derivatives **6** can also be conveniently prepared via a similar method to compound **5** from *N*-substituted α-substituted cyanoacetamides **4**. After this, according to the general method for synthesis of thiazolidine heterocycles, the ethyl 2-bromoacetate was used to construct the substituted thiazolidine **7** via sequence electrophilic substitution and intramolecular cyclization reactions. Furthermore, the intermediates **4** were used to react with appropriate aldehydes to give the corresponding heterocyclic 2*H*-1,3-thiazine derivatives **8** via classic heterocyclization reactions catalyzed by *p*-toluene sulfonic acid in the presence of ethanol. Irrespective of the fact whether aromatic or aliphatic aldehydes were used, the cyclization proceeded very smoothly in the same reaction conditions. All target compounds gave satisfactory chemical analyses, and the general procedures and spectral data were described in the Experimental section.

CONCLUSIONS

In summary, a convenient structural diversity-oriented synthesis of functionalized sulfur-containing heterocyclic scaffolds is described. The target isothiazole, 2*H*-1,3-thiazine, and thiazolidine heterocyclic derivatives have been prepared from α-substituted cyanoacetamides, which have been identified on the basis of analytical spectral data.

EXPERIMENTAL

Instrumentation and chemicals. All melting points (m.p.) were obtained using a digital model X-5 apparatus (Gongyi Yuhua Instrument Co., LTD, Gongyi, China) and are uncorrected. The infrared absorption spectra were recorded on a Thermo Nicolet FT-IR Avatar 330 instrument (Thermo Electron Corporation, Waltham, MA) in KBr discs and are reported in cm^{-1}. ^1H NMR spectra were recorded on a Brucker spectrometer (Bruker, Fallanden, Switzerland) at 400 MHz with DMSO-d_6 as the solvent and TMS as the internal standard. ^{13}C NMR spectra were recorded on a Brucker spectrometer at 150 MHz with DMSO-d_6 as solvent and TMS as the internal standard. Chemical shifts are reported in δ (parts per million) values. Coupling constants ^nJ are reported in Hz. Mass spectra were performed on a MicroMass Quattro *micro*™ API instrument (Waters, Milford, MA). Elemental analysis was performed on a Vario EL III elemental analysis instrument (Elementar Analysensysteme

GmbH, Germany). Analytical thin-layer chromatography (TLC) was carried out on precoated plates, and spots were visualized with ultraviolet light. All chemicals or reagents were purchased from standard commercial supplies, which were analytical grade and used directly without purification.

General synthetic procedure for the intermediate 3. To a solution of sodium hydroxide (0.4 g, 0.01 mol) in water (5 mL) was added carbon disulfide (1.14 g, 0.015 mol) under ice bath, and then substituted aromatic amine **1** (0.01 mol) was slowly added for about 30 min. After that, the ice bath was removed, and the mixture was rose to room temperature, and then the reaction mixture was heated to 70–80°C and monitored by TLC. After completion, the resulting mixture was cooled to room temperature, and the excess carbon disulfide was removed under vacuum distillation. Then, the residue was extracted by toluene, and the aqueous phase was directly used for the following transformation. To the obtained aqueous phase was added dropwise ethyl chloroformate (0.011 mol) under 30–35°C, and then the temperature of the mixture was maintained and detected by TLC. On completion of the reaction, the mixture was extracted with dichloromethane. The organic layer was washed with water and brine and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to obtain the products.

General synthetic procedure for the intermediate 4. To a stirring solution of cyanoacetamide (1.68 g, 0.02 mol) in 20 mL of *N*,*N*-dimethylacetamide was added 2.65 g (0.04 mol) of KOH powder. After 20 min, the newly prepared substituted isothiocyanate (0.015 mol) was added in 5 mL of *N*,*N*-dimethylacetamide. The mixture was stirred until the substituted isothiocyanate was disappeared, and then the reaction mixture was poured into ice water, and the pH value of the system was adjusted to 5–6. The mixture was stirred for additional 30 min, and the solid was separated after filtration, which were used directly without purification.

General synthetic procedure for substituted isothiazoles 5 and 6. The substituted isothiazole derivatives **5** and **6** were conveniently prepared via bromine oxidation reaction of compound **4**. The typical procedures are as follows: To a stirring solution of compound **4** (1 mmol) in 10 mL of ethyl acetate was added dropwise bromine (1.2 mmol in ethyl acetate). After 20 min stirring at ambient temperature, the solid was filtrated and washed with ethyl acetate.

3-Hydroxy-5-(phenylamino)isothiazole-4-carbonitrile 5a. White powder, yield 84%, m.p. 232–234°C; IR (KBr, cm^{-1}): υ 3284 (br, OH), 3125 (NH), 2158 (CN) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 10.67$ (s, 1H, NH), 7.42 (t, $J = 8$ Hz, 2H, Ph-H), 7.30 (d, $J = 8$ Hz, 2H, Ph-H), 7.19 (t, $J = 8$ Hz, 1H, Ph-H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 168.5, 165.7, 137.2, 133.8, 130.3, 125.6, 115.5, 81.4; MS (ESI) m/z 218.3 $(M+H)^+$, calcd for $C_{10}H_7N_3OS$ $m/z = 217.0$. *Anal*. Calcd for $C_{10}H_7N_3OS$: C, 55.29; H, 3.25; N, 19.34. Found: C, 55.10; H, 3.08; N, 19.52.

5-((6-Chloropyridin-3-yl)amino)-3-hydroxyisothiazole-4-carbonitrile 5b. White powder, yield 79%, m.p. >250°C; IR (KBr, cm^{-1}): υ 3316 (br, OH), 3150 (NH), 2172 (CN) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 10.82$ (s, 1H, NH), 8.41 (s, 1H, Py-H), 7.81 (dd, $J = 8.4$ Hz, 1H, Py-H), 7.57 (d, $J = 8.8$ Hz, 1H, Py-H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 161.3, 154.4, 145.2, 138.3, 134.5, 128.6, 126.4, 112.1, 89.6; MS (ESI) m/z 253.4 $(M+H)^+$, calcd for $C_9H_5ClN_4OS$ $m/z = 252.0$. *Anal*. Calcd for $C_9H_5ClN_4OS$: C, 42.78; H, 1.99; N, 22.17. Found: C, 42.52; H, 1.83; N, 22.33.

2-Cyclohexyl-3-oxo-5-(phenylamino)-2,3-dihydroisothiazole-4-carbonitrile 6a. White powder, yield 86%, m.p. 207–208°C; IR (KBr, cm^{-1}): υ 3138 (NH), 2183 (CN), 1647 (CO) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 10.94$ (s, 1H, NH), 7.45 (t, $J = 8$ Hz, 2H, Ph-H), 7.37–7.26 (m, 3H, Ph-H), 4.17–4.06 (m, 1H, N–CH), 1.83–1.65 (m, 4H, Cy-H), 1.61–1.49 (m, 1H, Cy-H), 1.43–1.22 (m, 4H, Cy-H), 1.15–1.01 (m, 1H, Cy-H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 169.2, 161.5, 135.4, 132.3, 128.1, 124.7, 117.6, 86.2, 63.8, 37.5, 27.4, 23.3; MS (ESI) m/z 300.6 $(M+H)^+$, calcd for $C_{16}H_{17}N_3OS$ $m/z = 299.1$. *Anal*. Calcd for $C_{16}H_{17}N_3OS$: C, 64.19; H, 5.72; N, 14.04. Found: C, 63.98; H, 5.87; N, 14.18.

5-((6-Chloropyridin-3-yl)amino)-2-cyclohexyl-3-oxo-2,3-dihydroisothiazole-4-carbonitrile 6b. White powder, yield 75%, m.p. 218–220°C; IR (KBr, cm^{-1}): υ 3148 (NH), 2189 (CN), 1654 (CO) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 11.04$ (s, 1H, NH), 8.47 (s, 1H, Py-H), 7.90 (q, $J = 8.4$ Hz, 1H, Py-H), 7.62 (d, $J = 8.8$ Hz, 1H, Py-H), 4.20–4.10 (m, 1H, N-CH), 1.82–1.73 (m, 4H, Cy-H), 1.65–1.50 (m, 1H, Cy-H), 1.45–1.31 (m, 4H, Cy-H), 1.20–1.05 (m, 1H, Cy-H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 171.4, 165.2, 139.5, 136.4, 131.5, 127.5, 125.2, 116.3, 89.6, 67.2, 39.3, 28.1, 23.9; MS (ESI) m/z 335.6 $(M+H)^+$, calcd for $C_{15}H_{15}ClN_4OS$ $m/z = 334.1$. *Anal*. Calcd for $C_{15}H_{15}ClN_4OS$: C, 53.81; H, 4.52; N, 16.73. Found: C, 53.64; H, 4.38; N, 16.81.

General synthetic procedure for substituted thiazolidine 7. The prepared intermediate **4** (1 mmol) was dissolved in dimethylformamide (8 mL), and the ethyl bromoacetate (1.2 mmol) was added. The reaction mixture was heated to 75–80°C for about 4–5 h, and the mixture was neutralized with saturated sodium carbonate solution, and ice water was added. The resulting precipitate was filtered off and recrystallized from ethanol.

2-Cyano-2-(4-oxo-3-phenylthiazolidin-2-ylidene)acetamide 7a. White powder, yield 77%, m.p. >250°C; IR (KBr, cm^{-1}): υ 3275, 3242 (NH), 2174 (CN), 1731, 1636 (CO) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 7.63$–7.57 (m, 4H, Ph-H), 7.48 (bs, 1H, NH), 7.32–7.27 (m, 1H, Ph-H), 7.11 (bs, 1H, NH), 3.88 (d, $^2J = 1.8$ Hz, 2H, CH_2); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.5, 161.4, 142.6, 137.1, 132.4, 128.6, 118.5, 88.2, 71.4, 40.2; MS (ESI) m/z 260.3 $(M+H)^+$, calcd for $C_{12}H_9N_3O_2S$ $m/z = 259.0$. *Anal*.

Calcd for $C_{12}H_9N_3O_2S$: C, 55.59; H, 3.50; N, 16.21. Found: C, 55.43; H, 3.36; N, 16.37.

2-(3-(6-Chloropyridin-3-yl)-4-oxothiazolidin-2-ylidene)-2-cyanoacetamide 7b. White powder, yield 73%, m.p. >250°C; IR (KBr, cm^{-1}): υ 3316, 3274 (NH), 2186 (CN), 1748, 1644 (CO) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 8.53$ (d, $J = 4$ Hz, 1H, Py-H), 8.02 (q, $J = 8$ Hz, 1H, Py-H), 7.75 (d, $J = 8$ Hz, 1H, Py-H), 7.44 (bs, 1H, NH), 7.07 (bs, 1H, NH), 3.92 (d, $^2J = 1.6$ Hz, 2H, CH_2); ^{13}C NMR (150 MHz, DMSO-d_6): δ 169.3, 164.5, 143.1, 140.2, 137.8, 133.5, 126.2, 120.4, 92.6, 73.5, 43.6; MS (ESI) m/z 295.4 $(M+H)^+$, calcd for $C_{11}H_7ClN_4O_2S$ $m/z = 294.0$. *Anal*. Calcd for $C_{11}H_7ClN_4O_2S$: C, 44.83; H, 2.39; N, 19.01. Found: C, 44.58; H, 2.27; N, 19.32.

General synthetic procedure for 1,3-thiazine 8. To a solution of α-substituted cyanoacetamides **4** (1 mmol) in anhydrous ethanol (15 mL) was added corresponding aldehyde (1.1 mmol) and catalytic amount of *p*-toluenesulfonic acid at room temperature, and then the stirred mixture was refluxed for several hours, which was monitored by TLC. Then the solution was concentrated, and the heterocyclization products **8** separated out on cooling and were recrystallized from aqueous ethanol.

2-Ethyl-4-oxo-6-(phenylamino)-3,4-dihydro-2H-1,3-thiazine-5-carbonitrile 8a. Pale yellowish solid, yield 83%, m.p. 225–227°C; IR (KBr, cm^{-1}): υ 3352, 3314 (NH), 2195 (CN), 1723, 1678 (CO) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 10.42$ (s, 1H, NH), 8.56 (s, 1H, NH), 7.48 (t, $J = 8$ Hz, 2H, Ph-H), 7.38–7.27 (m, 3H, Ph-H), 4.81 (t, $J = 8.4$ Hz, 1H, S-CH), 2.38 (m, 2H, CH_2), 1.14 (t, $J = 8$ Hz, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ 167.6, 164.3, 139.1, 130.2, 127.3, 125.4, 119.4, 82.7, 59.6, 37.5, 10.8; MS (ESI) m/z 260.6 $(M+H)^+$, calcd for $C_{13}H_{13}N_3OS$ $m/z = 259.1$. *Anal*. Calcd for $C_{13}H_{13}N_3OS$: C, 60.21; H, 5.05; N, 16.20. Found: C, 60.03; H, 4.90; N, 16.41.

4-Oxo-2-phenyl-6-(phenylamino)-3,4-dihydro-2H-1,3-thiazine-5-carbonitrile 8b. Pale yellowish solid, yield 74%, m.p. >50°C; IR (KBr, cm^{-1}): υ 3346, 3298 (NH), 2210 (CN), 1704, 1658 (CO) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 10.48$ (s, 1H, NH), 8.62 (s, 1H, NH), 7.65–7.48 (m, 7H, Ph-H), 7.25–7.18 (m, 3H, Ph-H), 5.68 (s, 1H, S–CH); ^{13}C NMR (150 MHz, DMSO-d_6): δ 168.1, 165.7, 142.4, 138.3, 132.5, 129.6, 127.4, 125.8, 124.2, 121.7, 115.2, 89.4, 62.3; MS (ESI) m/z 308.4 $(M+H)^+$, calcd for $C_{17}H_{13}N_3OS$ $m/z = 307.1$. *Anal*. Calcd for $C_{17}H_{13}N_3OS$: C, 66.43; H, 4.26; N, 13.67. Found: C, 66.25; H, 4.08; N, 13.84.

6-((6-Chloropyridin-3-yl)amino)-2-ethyl-4-oxo-3,4-dihydro-2H-1,3-thiazine-5-carbonitrile 8c. Pale yellowish solid, yield 87%, m.p. 243–245°C; IR (KBr, cm^{-1}): υ 3368, 3327 (NH), 2208 (CN), 1716, 1663 (CO) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 10.71$ (s, 1H, NH), 8.73 (s, 1H, NH), 8.36 (s, 1H, Py-H), 7.72 (dd, $J = 8$ Hz, 1H, Py-H), 7.51 (d, $J = 8$ Hz, 1H, Py-H), 4.86 (t, $J = 8$ Hz, 1H, S–CH), 2.35 (m, 2H, CH_2), 1.08 (t, $J = 8$ Hz, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ 171.3, 166.4, 158.6, 142.4, 138.6, 128.1, 125.7, 118.3, 86.8, 57.2, 38.6, 10.5; MS (ESI) m/z 295.5 $(M+H)^+$, calcd for $C_{12}H_{11}ClN_4OS$ $m/z = 294.0$. *Anal*. Calcd for $C_{12}H_{11}ClN_4OS$: C, 48.90; H, 3.76; N, 19.01. Found: C, 48.69; H, 3.62; N, 19.26.

6-((6-Chloropyridin-3-yl)amino)-4-oxo-2-phenyl-3,4-dihydro-2H-1,3-thiazine-5-carbonitrile 8d. Pale yellowish solid, yield 81%, m.p. >250°C; IR (KBr, cm^{-1}): υ 3359, 3318 (NH), 2202 (CN), 1712, 1668 (CO) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 10.78$ (s, 1H, NH), 8.67 (s, 1H, NH), 8.40 (s, 1H, Py-H), 7.85–7.62 (m, 6H, Py-H and Ph-H), 7.56 (d, $J = 8$ Hz, 1H, Py-H), 5.73 (s, 1H, S–CH); ^{13}C NMR (150 MHz, DMSO-d_6): δ 170.2, 167.5, 156.4, 144.6, 140.3, 137.4, 130.5, 128.4, 126.6, 122.4, 120.1, 116.8, 91.6, 65.7; MS (ESI) m/z 343.4 $(M+H)^+$, calcd for $C_{16}H_{11}ClN_4OS$ $m/z = 342.0$. *Anal*. Calcd for $C_{16}H_{11}ClN_4OS$: C, 56.06; H, 3.23; N, 16.34. Found: C, 49.83; H, 3.05; N, 16.52.

Acknowledgments. This work was supported in part by the Applied Basic Research Program of Wuhan City (2016020101010093) and Hubei Agricultural Science Innovation Centre (2016-620-000-001-039). The authors also gratefully acknowledge the partial support from the Key Laboratory of Integrated Pest Management in Crops in Central China, Ministry of Agriculture and Key Laboratory for Crop Diseases, Insect Pests and Weeds Control in Hubei Province (2015ZTSJJ9).

REFERENCES AND NOTES

[1] Bernardi, F.; Csizmadia, I. G.; Mangini, A. Organic Sulfur Chemistry. Theoretical and Experimental Advances, 19, Elsevier, Amsterdam, 1985.

[2] Hassan, A. A.; EI-Sheref, E. M. J Heterocyclic Chem 2010, 47, 764.

[3] Bregović, V. B.; Basarić, N.; Mlinarić-Majerski, K. Coord Chem Rev 2015, 295, 80.

[4] Peng, H.; Chen, W.; Cheng, Y.; Hakuna, L.; Strongin, R.; Wang, B. Sensors 2012, 12, 15907.

[5] Liu, H.; Jiang, X. Chem Asian J 2013, 8, 2546.

[6] Saeed, A.; Flörke, U.; Erben, M. F. J Sulfur Chem 2014, 35, 318.

[7] Gonzalez-Estrada, A.; Radojicic, C. Clev Clin J Med 2015, 82, 295.

[8] Vree, T. B. Antibiot Chemother Basel Karger 1987, 37, 155.

[9] Takayama, S.; Sieber, S. M.; Adamson, R. H.; Thorgeirsson, U. P.; Dalgard, D. W.; Arnold, L. L.; Cano, M.; Eklund, S.; Cohen, S. M. J Natl Cancer Inst 1998, 90, 19.

[10] Kim, T. H.; Jeong, J. W.; Song, J. H.; Lee, K. R.; Ahn, S.; Ahn, S. H.; Kim, S.; Koo, T. S. Arch Pharm Res 2015, 38, 2076.

[11] Zhang, Q. World Pestic 2009, 31, 53.

[12] Chen, X.; Wang, D.; Huang, J.; Huang, Y.; Fan, Z. China Agrochem 2012, 1, 31.

[13] Ni, C. World Pestic 2007, 29, 18.

[14] Jeschke, P.; Nauen, R.; Schindler, M.; Elbert, A. J Agric Food Chem 2011, 59, 2897.

[15] Oka, Y. Pest Manag Sci 2014, 70, 1850.

[16] Ram, V. J.; Srivastava, P.; Goel, A. Tetrahedron 2003, 59, 7141.

[17] Lebedyeva, I. O.; Dotsenko, V. V.; Turovtsev, V. V.; Krivokolysko, S. G.; Povstyanoy, V. M.; Povstyanoy, M. V. Tetrahedron 2012, 68, 9729.

[18] Bedane, K. G.; Singh, G. S. ARKIVOC 2015, vi, 206.

[19] Kabirifard, H.; Ghahremani, S.; Afsharpoor, A. J Sulfur Chem 2015, 36, 591.

[20] Munch, H.; Hansen, J. S.; Pittelkow, M.; Christensen, J. B.; Boas, U. Tetrahedron Lett 2008, 49, 3117.

[21] Chaskar, A. C.; Yewale, S.; Bhagat, R.; Langi, B. P. Synth Commun 2008, 38, 1972.

[22] Florence, X.; Sebille, S.; de Tullio, P.; Lebrun, P.; Pirotte, B. Bioorg Med Chem 2009, 17, 7723.

[23] Misra, A.; Shahid, M.; Dwivedi, P. Talanta 2009, 80, 532.

[24] Cee, V. J.; Frohn, M.; Lanman, B. A.; Goden, J.; Muller, K.; Neira, S.; Pickrell, A.; Arnett, H.; Buys, J.; Gore, A.; Fiorino, M.; Horner, M.; Itano, A.; Lee, M. R.; McElvain, M.; Middleton, S.; Schrag, M.; Rivenzon-Segal, D.; Vargas, H. M.; Xu, H.; Xu, Y.; Zhang, X.; Siu, J.; Wong, M.; Bürli, R. W. ACS Med Chem Lett 2011, 2, 107.

[25] Sun, N.; Li, B.; Shao, J.; Mo, W.; Hu, B.; Shen, Z.; Hu, X. Beilstein J Org Chem 2012, 8, 61.