Organic & Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2021, **19**, 5108

NH_4I-promoted oxidative formation of benzothiazoles and thiazoles from arylacetic acids and phenylalanines with elemental sulfur†

Yujia Xia, Huawen Huang, * Wei Hu and Guo-Jun Deng *

Received 7th April 2021,
Accepted 12th May 2021

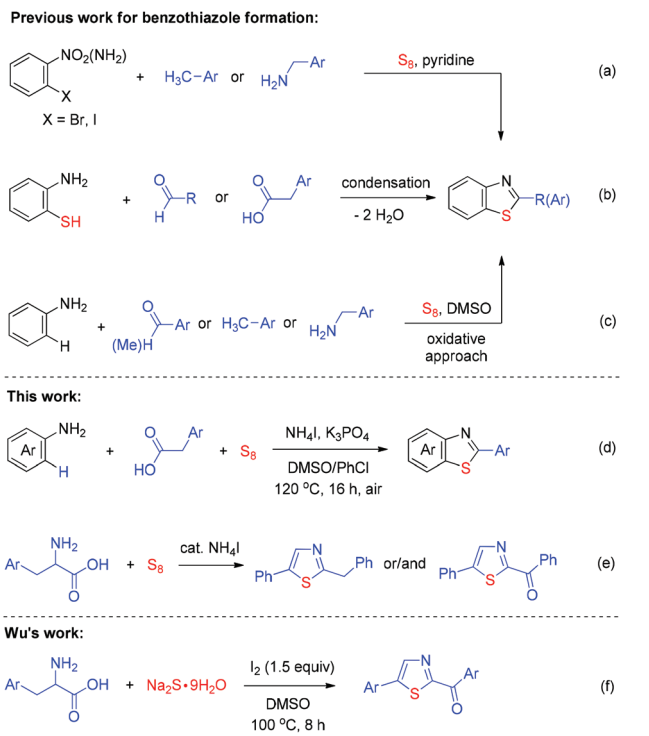
DOI: 10.1039/d1ob00671a

rsc.li/obc

A NH_4I/K_3PO_4-based catalytic system has been established to enable oxidative formation of thiazole compounds from arylacetic acids and phenylalanines with elemental sulfur. While the three-component reaction of anilines or β-naphthylamines with arylacetic acids and elemental sulfur affords benzo[2,1-*d*]thiazoles and naphtho[2,1-*d*]thiazoles, the annulation of phenylalanines with elemental sulfur produces 2-benzyl and 2-benzoylthiazoles. This work well complements previous three-component annulations of benzothiazoles from other coupling partners.

Introduction

Structurally privileged thiazole compounds have widely been exploited in pharmaceuticals,[1] naturally occurring products,[2] and functional materials.[3] These practical applications have intensively triggered the structural and synthetic development of this skeleton motif. While various cyclization reactions have been discovered to construct the key thiazole ring,[4] more specifically, traditional methods to synthesize benzothiazoles mainly depend on condensation and coupling reactions of pre-functionalized *ortho* disubstituted arenes such as *ortho*-halo anilines or nitroarenes (Scheme 1(a)) and 2-aminobenzenethiols (Scheme 1(b)).[5] With user-friendly elemental sulfur as a building block for sulfur–heterocycle formation,[6] our group and others have developed direct C–H sulfuration of β-naphthylamines and anilines that leads to highly efficient annulations of 2-arylbenzothiazoles and 2-arylnaphthothiazoles under facile transition-metal-free conditions,[7] in which benzaldehydes,[7a,f] methylheteroarenes,[7b,c] benzylamines,[7e] and acetophenones[7g] were all effective C1 sources (Scheme 1(c)). Our reaction with benzaldehyde was recently used to produce stable thiazole-linked material molecules of covalent organic frameworks (COFs), which were found to feature high sacrificial hydrogen evolution rates from water under photocatalysis.[8] Although significant utility has been primarily established, this method still has limitations. For example, aniline compounds exhibited low reactivity, even at a very high reaction temperature (150 °C). Hence, to improve the reactivity of C–H sulfuration of anilines for thiazole annulations, we speculate that a variant of the aldehyde coupling partner as a C1 source as well as a new catalytic systems may be exploited. Inspired by the multicomponent decarboxylative reaction of sulfur, carboxylic acids, and amines,[9] herein, we



Scheme 1 Methods for benzothiazole formation.

Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China. E-mail: gjdeng@xtu.edu.cn, hwhuang@xtu.edu.cn; Fax: (+86)0731-58292251; Tel: (+86)0731-58298601

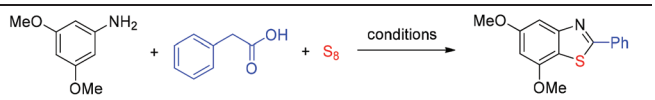
†Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ob00671a

explore phenylacetic acids as the coupling partner for the efficient thiazo-annulation of anilines (Scheme 1(d)). Further studies reveal that the corresponding amino acids could play the same role of a C1 source, while phenylalanines undergo two-component thiazo-annulation with elemental sulfur to produce two kinds of 2,5-disubstituted thiazole products (Scheme 1(e)). In 2018, Wu and coworkers developed an iodine-promoted cyclization reaction of phenylalanine with Na_2S as the sulfur source, affording only benzoyl thiazole products while elemental sulfur did not work in that system (Scheme 1(f)).[10]

Results and discussion

In related reports, sp^2 C–H sulfuration with elemental sulfur occurred normally with electron-rich arenes,[7] thereby electrophilic substitution was mechanistically proposed. To commence our study, 3,4-dimethoxyaniline (**1a**) and phenylacetic acid (**2a**) were used as model substrates to optimize the reaction conditions (Table 1). In the absence of a base, the KI/NMP system, which has been demonstrated to be effective with benzaldehydes, did not work for the present cyclization (entry 1). As a comparison, the NH_4I/DMSO/PhCl-based catalytic system gave modest yield of the desired benzothiazole product **3a** (entry 2). The addition of a base could facilitate the decarboxylation process of carboxylic acids as well as activation of elemental sulfur to form S_3 radical anions ($S_3^{\bullet-}$).[11] Hence, a series of inorganic bases were screened (entries 3–7). Of them, while NaOEt completely quenched the annulation reaction, others including K_2CO_3, K_3PO_4, NaOH, and Cs_2CO_3 were all effective and K_3PO_4 gave the best result (82% yield, entry 4). Then, the solvent effect was explored. DMSO was found to be critical to the C–H sulfuration reaction. While PhCl enables the reaction with 20% yield (entry 8), other solvents such as NMP, 1,4-dioxane, and toluene did not work at all (entries 10–12). As previously obtained in the case of aldehydes as the coupling partner, the combinational use of DMSO and PhCl (v/v = 1 : 3) proved superior (entry 9). These results indicate that DMSO probably plays a dual role of both a solvent and an oxidant or an activating reagent. Unexpectedly, elemental iodine did not work or prohibit the present annulation reaction (entry 13) because the reaction in the absence of a catalyst also afforded **3a** in moderate yield (entry 14). The reaction yield was slightly declined when reducing the catalyst loading to 5 mol% (entry 15). Notably, the reaction yield was dramatically decreased either at lowered or elevated temperature (entries 16 and 17). Finally, oxygen in air proved to be helpful since an inert atmosphere reduced the yield to 77% (entries 18 and 19).

Table 1 Optimization of reaction conditions[a]



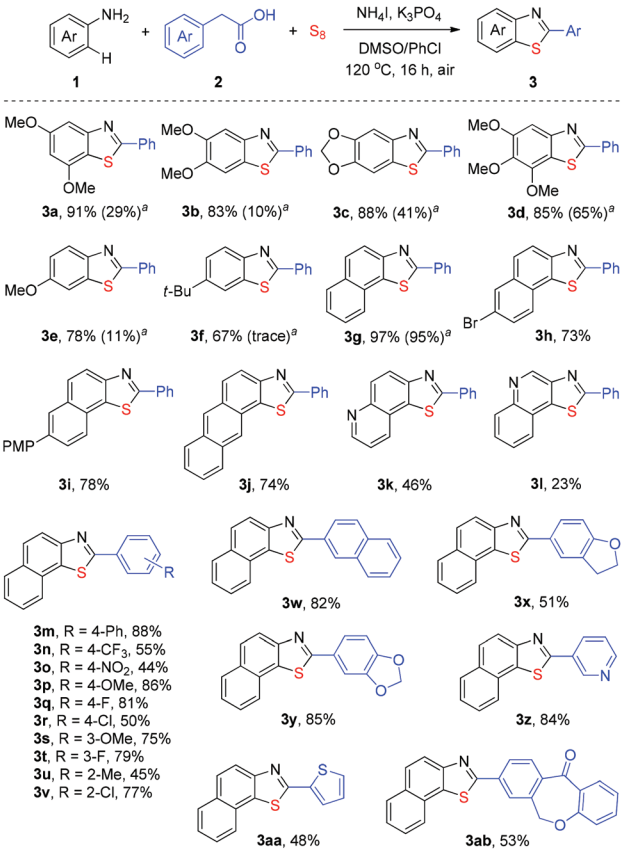
1a **2a** **3a**

Entry	Catalyst (mol%)	Base	Solvent	Yield[b] (%)
1	KI (20)		NMP	ND
2	NH_4I (10)		DMSO/PhCl	55
3	NH_4I (10)	K_2CO_3	DMSO	71
4	NH_4I (10)	K_3PO_4	DMSO	82
5	NH_4I (10)	NaOH	DMSO	65
6	NH_4I (10)	NaOEt	DMSO	—
7	NH_4I (10)	Cs_2CO_3	DMSO	70
8	NH_4I (10)	K_3PO_4	PhCl	20
9	NH_4I (10)	K_3PO_4	DMSO/PhCl	91
10	NH_4I (10)	K_3PO_4	1,4-Dioxane	—
11	NH_4I (10)	K_3PO_4	NMP	—
12	NH_4I (10)	K_3PO_4	Toluene	—
13	I_2 (10)	K_3PO_4	DMSO/PhCl	Trace
14	—	K_3PO_4	DMSO/PhCl	60
15	NH_4I (5)	K_3PO_4	DMSO/PhCl	88
16[c]	NH_4I (10)	K_3PO_4	DMSO/PhCl	64
17[d]	NH_4I (10)	K_3PO_4	DMSO/PhCl	50
18[e]	NH_4I (10)	K_3PO_4	DMSO/PhCl	90
19[f]	NH_4I (10)	K_3PO_4	DMSO/PhCl	77

[a] The reactions were performed with **1a** (0.2 mmol), **2a** (0.2 mmol), S_8 (1.0 mmol, 32 g mol^{-1}), catalyst (mol%), and base (1.0 equiv.) in solvent (1 mL) under air for 16 h. [b] Yields of isolated product **3a** are given. [c] 140 °C. [d] 100 °C. [e] Charged with O_2 (sealed tube). [f] Charged with Ar.

With the optimal reaction conditions in hand, the substrate scope of the three-component annulation reaction was probed (Scheme 2). Anilines bearing electron-donating functional groups including methoxy and *tert*-butyl were smoothly cyclized, generating the corresponding benzothiazoles in good to excellent yields (**3a–3f**, 67%–91% yields). Electron-deficient anilines only afforded the possible imine and thioamide intermediate products under the present catalytic system. As expected, β-naphthylamines as well as β-anthramine featured high reactivity (**3g–3j**, 74%–97% yields), with bromo functionality well tolerated (**3h**). Quinolin-6-amine and quinolin-3-amine were also productive, albeit in low yields. Subsequently, with β-naphthylamine as the coupling partner the generality of arylacetic acids was explored. Generally, substituted phenylacetic acids produce the target 2-arylnaphtho[2,1-*d*]thiazoles in moderate to excellent yields (**3m–3v**, 45%–88% yields), although their yields are to some extent lower than those of our previous systems with aldehydes. A broad range of useful functional groups such as nitro, methoxyl, fluoro, chloro, and bromo are all compatible with the current system. 2-(Naphthalen-2-yl)acetic acid worked well to afford **3w** in 82% yield. Other fused arylacetic acids with tetrahydrofuran and the dioxolane moiety delivered the corresponding naphtho[2,1-*d*]thiazoles **3x** and **3y** in 51% and 85% yields, respectively. The reactivity of heteroarylacetic acids was exemplified by pyridinyl and thienyl coupling partners, which furnished the expected biheteroarene products (**3z** 84%, **3aa** 48%). Notably, isoxepac, a non-steroidal anti-inflammatory drug, was also an effective substrate, generating the structurally significant naphthothiazole-attached dibenzo[*b*,*e*]oxepin-11(6*H*)-one **3ab**.

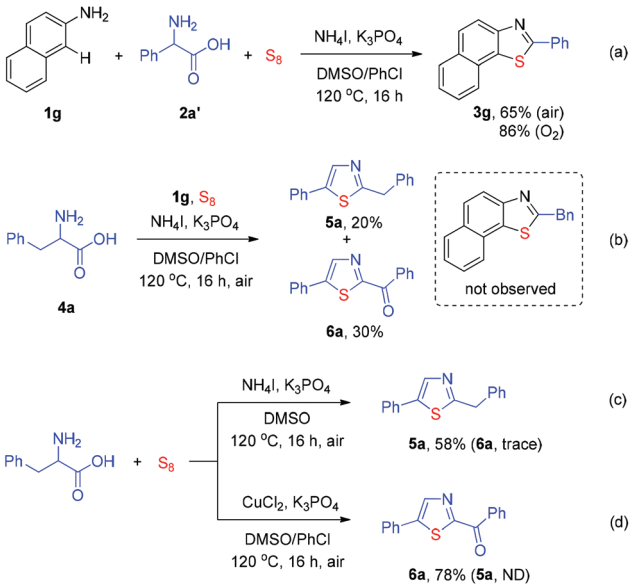
Amino acids are readily available biomass and have been widely exploited as building blocks in molecule synthesis. To our delight, 2-amino-2-phenylacetic acid (**2a′**) could be



Scheme 2 Substrate scope of benzothiazole formation ([a] yields with the use of benzaldehyde instead of phenylacetic acid are given in parentheses).

employed to replace phenylacetic acid in our three-component cyclization reaction. The reaction with β-naphthylamine under standard conditions afforded 2-phenylnaphtho[2,1-*d*]thiazole **3g** in 65% yield, with highly enhanced reactivity under an oxygen atmosphere (86% yield) (Scheme 3a). Unexpectedly, when phenylalanine (**4a**) was used, the β-naphthylamine component did not participate in the reaction. Instead, two molecules of **4a** reacted with elemental sulfur to produce benzyl- and benzoyl thiazole products **5a** and **6a**, respectively (Scheme 3b). Previously, Wu and coworkers developed an iodine-promoted cyclization reaction of phenylalanine with Na_2S as the sulfur source, affording only benzoyl thiazole products while elemental sulfur did not work in that system.[10] Complementary to this work, we modified the reaction conditions for both thiazole formations. Reducing the amount of K_3PO_4 seemed to be the key for the formation of the "non-oxidative" product **5a**. Notably, prolonged reaction time could lead to significant formation of 2-benzoylthiazoles. Then, the use of copper catalyst instead of NH_4I completely turned the chemoselectivity over the 2-benzoyl product (Scheme 3c and d).

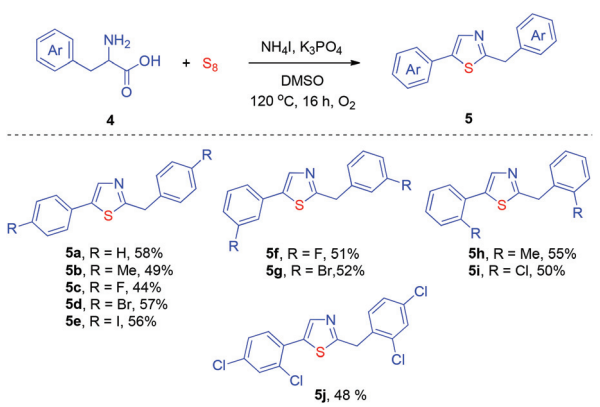
Thereafter, we explored the substrate scope of benzylthiazole formation by using a range of substituted phenylalanines. Generally, the 2-benzoylthiazole products were formed in moderate yields. Halogens including fluoro, chloro, bromo, and



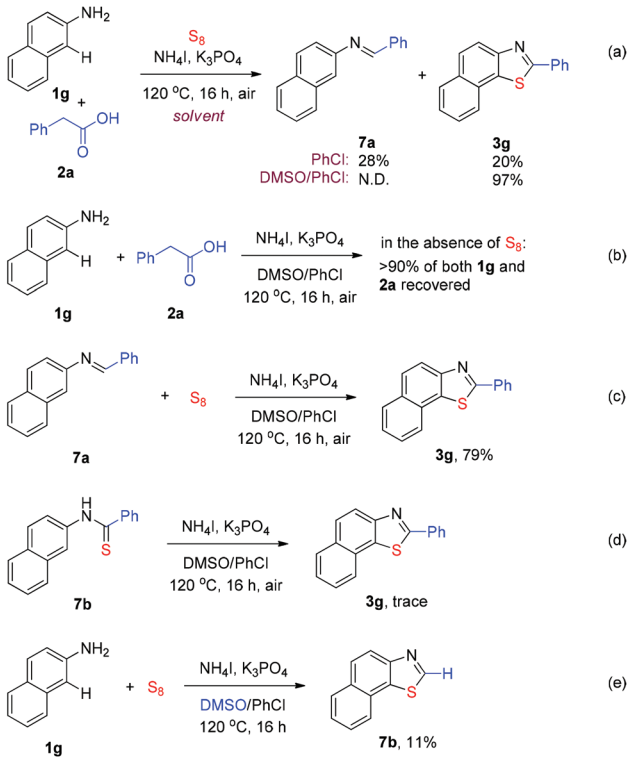
Scheme 3 Reactivity of amino acids.

iodine were all accommodated with the NH_4I/K_3PO_4 system (Scheme 4).

To gain mechanistic insight into the sulfuration/annulations with arylacetic acids, some control experiments were carried out (Scheme 5). When the co-solvent DMSO was removed, the reaction of β-naphthylamine **1g** and phenylacetic acid **2a** afforded **3g** in only 20% yield, along with the possible imine intermediate product **7a** (28%). This result suggests that DMSO could promote both oxidative decarboxylation and thiazo-annulation (Scheme 5a). Both **1g** and **2a** were recovered in the absence of elemental sulfur, revealing oxidative decarboxylation enabled by elemental sulfur (Scheme 5b). The imine **7a** smoothly transformed into a naphtho[2,1-*d*]thiazole product (Scheme 5c), while only a trace amount of product was detected when *N*-(naphthalen-2-yl)benzothioamide was employed (Scheme 5d). Finally, the C–H sulfuration and thiazo-annulation of β-naphthylamine also occurred in the absence of phenylacetic acid **2a**, where DMSO probably served



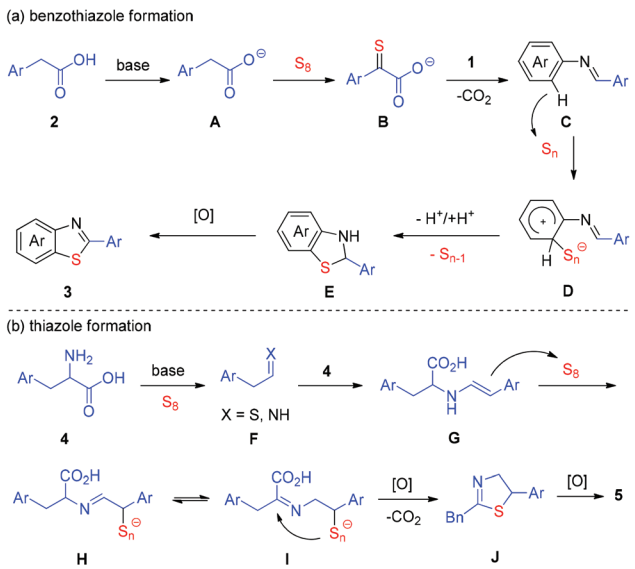
Scheme 4 Substrate scope of benzylthiazole formation.



Scheme 5 Control experiments.

as the C1 source to enable the formation of naphtho[2,1-*d*]thiazole **7b** (Scheme 5e).

On the basis of our experimental results and literature reports,[7a,9a] we proposed a possible reaction mechanism of thiazo-annulations (Scheme 6). First, the deprotonation of phenylacetic acid **2** occurs to give acetate **A**, which undergoes Willgerodt–Kindler-type sulfuration to generate thioxoacetic acid **B**.[12] The intermediate **B** condenses with arylamine followed by decarboxylation to afford imine **C**. Then, *ortho* electrophilic sulfuration of **C** with elemental sulfur leads to intermediate **D**, with a sequential deprotonation/nucleophilic cyclization/protonation process to give dihydrobenzothiazole **E**. Finally, oxidative dehydrogenative aromatization of **E** furnishes benzothiazole product **3**. With regard to the thiazole formation from phenylalanines (Scheme 6b),[11] the initial step should be oxidative decarboxylation of **4**, which probably produces imine or ethanethial **F**. Condensation of **F** with another molecule of phenylalanine gives enamine intermediate **G**. Again, Willgerodt–Kindler-type sulfuration of **G** with elemental sulfur happens to generate polysulfur intermediate **H**, with tautomerism to form imine **I**. Subsequently, intramolecular nucleophilic attack of sulfur anions on imine moieties, along with oxidative decarboxylation, delivers dihydrothiazole **J**, with the final dehydrogenative oxidation to form 2-benzyl-5-arylthiazole product **5**.



Scheme 6 Possible reaction mechanism.

Conclusions

In summary, we have developed NH_4I-promoted benzothiazole formation from anilines, arylacetic acids, and elemental sulfur. This protocol provides an alternative access to valuable benzo- and naphtho[2,1-*d*]thiazole compounds from inexpensive and bench-stable starting materials. Arylacetic acids could also be replaced by the corresponding amino acid biomass. Moreover, benzyl- and benzoyl thiazole products were unexpectedly produced when phenylalanine was used, which well complements the iodine-promoted benzoylthiazole formation with Na_2S.

Experimental

General information

All reactions were carried out under an air atmosphere. Column chromatography was performed using silica gel (200–300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-AV (400, 100 and 376 MHz, respectively) instrument internally referenced to tetramethyl silane (TMS) or chloroform signals. Mass spectra were measured on an Agilent 5977 GC-MS instrument (EI). High-resolution mass spectra (HRMS) were recorded on an Agilent 6230 TOF LC/MS. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of the literature. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. Starting materials were obtained from commercial suppliers and used without further purification.

General procedure for the synthesis of benzothiazoles

A 10 mL reaction vessel was charged with NH_4I (0.04 mmol, 0.2 equiv.), K_3PO_4 (0.2 mmol, 1.0 equiv.), arylamine (**1**,

0.2 mmol, 1.0 equiv.), aryl acetic acid (**2**, 0.3 mmol, 1.5 equiv.), and sulfur (1.0 mmol, 5.0 equiv.). DMSO (0.25 mL) and chlorobenzene (0.75 mL) were added to the sealed reaction vessel using a syringe. The resulting solution was stirred at 120 °C for 16 h. The mixture was then allowed to cool down to room temperature and flushed through a short column of silica gel with ethyl acetate. After rotary evaporation, the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc = 10 : 1 to 20 : 1) to give benzothiazoles **3**.

General procedure for the synthesis of 2,5-disubstituted thiazoles

A 10 mL reaction vessel was charged with NH_4I (0.04 mmol, 0.2 equiv.), K_3PO_4 (0.1 mmol, 0.5 equiv.), phenylalanine (**4**, 0.4 mmol, 2.0 equiv.), and sulfur (1.0 mmol, 5.0 equiv.). DMSO (1.0 mL) was added to the sealed reaction vessel using a syringe. The resulting solution was stirred at 120 °C for 16 h. The mixture was then allowed to cool down to room temperature and flushed through a short column of silica gel with ethyl acetate. After rotary evaporation, the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc = 10 : 1 to 20 : 1) to give 2,5-disubstituted thiazoles **5**.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

Support from the National Natural Science Foundation of China (21871226 and 22071211), the Science and Technology Planning Project of Hunan Province (2019RS2039), the Hunan Provincial Natural Science Foundation of China (2020JJ3032), and the Collaborative Innovation Center of New Chemical Technologies for Environmental Benignity and Efficient Resource Utilization is gratefully acknowledged.

Notes and references

1 (*a*) T. Seiser, F. Kamena and N. Cramer, *Angew. Chem., Int. Ed.*, 2008, **47**, 6483–6485; (*b*) A. Dondoni, *Org. Biomol. Chem.*, 2010, **8**, 3366–3385; (*c*) S. Schoof, G. Pradel, M. N. Aminake, B. Ellinger, S. Baumann, M. Potowski, Y. Najajreh, M. Kirschner and H. D. Arndt, *Angew. Chem., Int. Ed.*, 2010, **49**, 3317–3321; (*d*) M. S. Alam, L. Liu, Y.-E. Lee and D.-U. Lee, *Chem. Pharm. Bull.*, 2011, **59**, 568–573; (*e*) H. Mohammad, A. S. Mayhoub, A. Ghafoor, M. Soofi, R. A. Alajlouni, M. Cushman and M. N. Seleem, *J. Med. Chem.*, 2014, **57**, 1609–1615; (*f*) T. Tomašič, S. Katsamakas, Ž. Hodnik, J. Ilaš, M. Brvar, T. Solmajer, S. Montalvão, P. Tammela, M. Banjanac, G. Ergović, M. Anderluh, L. P. Mašič and D. Kikelj, *J. Med. Chem.*, 2015, **58**, 5501–5521.

2 (*a*) Z. Jin, *Nat. Prod. Rep.*, 2003, **20**, 584–605; (*b*) D. Davyt and G. Serra, *Mar. Drugs*, 2010, **8**, 2755–2780; (*c*) X. Just-Baringo, P. Bruno, L. K. Ottesen, L. M. Canedo, F. Albericio and M. Alvarez, *Angew. Chem., Int. Ed.*, 2013, **52**, 7818–7821; (*d*) Z. E. Wilson, S. Fenner and S. V. Ley, *Angew. Chem., Int. Ed.*, 2015, **54**, 1284–1288; (*e*) K. P. Wojtas, M. Riedrich, J.-Y. Lu, P. Winte, T. Winkler, S. Walter and H.-D. Arndt, *Angew. Chem., Int. Ed.*, 2016, **55**, 9772–9776.

3 (*a*) P. Jiang, G. M. Morales, W. You and L. Yu, *Angew. Chem., Int. Ed.*, 2004, **43**, 4471–4475; (*b*) A. Wakamiya, T. Taniguchi and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2006, **45**, 3170–3173; (*c*) K. Mouri, S. Saito and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2012, **51**, 5971–5975; (*d*) M. Herder, F. Eisenreich, A. Bonasera, A. Grafl, L. Grubert, M. Pätzel, J. Schwarz and S. Hecht, *Chem. – Eur. J.*, 2017, **23**, 3743–3754; (*e*) C. J. Martin, M. Minamide, J. P. D. C. Calupitan, R. Asato, J. Kuno, T. Nakashima, G. Rapenne and T. Kawai, *J. Org. Chem.*, 2018, **83**, 13700–13706.

4 (*a*) F. Asinger and H. Offermanns, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 907; (*b*) G. K. Musorin, *Russ. J. Gen. Chem.*, 2002, **72**, 325; (*c*) K. K. Childers, A. M. Haidle, M. R. Machacek, J. P. Rogers and E. Romeo, *Tetrahedron Lett.*, 2013, **54**, 2506–2510; (*d*) P. Jiang, X. Che, Y. Liao, H. Huang and G.-J. Deng, *RSC Adv.*, 2016, **6**, 41751–41754; (*e*) X. Wang, X. Qiu, J. Wei, J. Liu, S. Song, W. Wang and N. Jiao, *Org. Lett.*, 2018, **20**, 2632–2636; (*f*) M. Wu, Y. Jiang, Z. An, Z. Qi and R. Yan, *Adv. Synth. Catal.*, 2018, **360**, 4236–4240; (*g*) G. Wu, R. Zheng, J. Nelson and L. Zhang, *Adv. Synth. Catal.*, 2014, **356**, 1229–1234; (*h*) J. Xu, R. Deng, J. Chen, X. Tang and J. Zhao, *Adv. Synth. Catal.*, 2019, **361**, 5144–5148.

5 (*a*) T. B. Nguyen, L. Ermolenko and A. Al-Mourabit, *Org. Lett.*, 2013, **15**, 4218–4221; (*b*) T. B. Nguyen, L. Ermolenko, P. Retailleau and A. Al-Mourabit, *Angew. Chem., Int. Ed.*, 2014, **53**, 13808–13812; (*c*) T. B. Nguyen, K. Pasturaud, L. Ermolenko and A. Al-Mourabit, *Org. Lett.*, 2015, **17**, 2562–2565; (*d*) M. Wang, Q. Fan and X. Jiang, *Org. Lett.*, 2016, **18**, 5756–5759; (*e*) J. Ying, H. Wang, X. Qi, J.-B. Peng and X.-F. Wu, *Eur. J. Org. Chem.*, 2017, 688–692; (*f*) X. Zhu, Y. Yang, G. Xiao, J. Song, Y. Liang and G. Deng, *Chem. Commun.*, 2017, **53**, 11917–11920.

6 (*a*) H. Liu and X. Jiang, *Chem. – Asian J.*, 2013, **8**, 2546–2563; (*b*) T. B. Nguyen, *Adv. Synth. Catal.*, 2017, **359**, 1066–1130; (*c*) H. Huang, G.-J. Deng and S. Liu, *Synlett*, 2020, **32**, 142–158; (*d*) T. B. Nguyen, *Adv. Synth. Catal.*, 2020, **362**, 3448–3484.

7 (*a*) X. Che, J. Jiang, F. Xiao, H. Huang and G.-J. Deng, *Org. Lett.*, 2017, **19**, 4576–4579; (*b*) G. Li, H. Xie, J. Chen, Y. Guo and G.-J. Deng, *Green Chem.*, 2017, **19**, 4043–4047; (*c*) H. Huang, Q. Wang, Z. Xu and G. J. Deng, *Adv. Synth. Catal.*, 2018, **361**, 591–596; (*d*) J. Jiang, G. Li, F. Zhang, H. Xie and G.-J. Deng, *Adv. Synth. Catal.*, 2018, **360**, 1622–1627; (*e*) X. Zhu, F. Zhou, Y. Yang, G. Deng and Y. Liang, *ACS Omega*, 2020, **5**, 13136–13147; (*f*) W. Chen, X. Zhu, F. Wang, Y. Yang, G. Deng and Y. Liang, *J. Org. Chem.*,

2020, **85**, 3349–3357; (*g*) Y. Liu, X. Yuan, X. Guo, X. Zhang and B. Chen, *Tetrahedron*, 2018, **74**, 6057–6062.

8 K. Wang, Z. Jia, Y. Bai, X. Wang, S. E. Hodgkiss, L. Chen, S. Y. Chong, X. Wang, H. Yang, Y. Xu, F. Feng, J. W. Ward and A. I. Cooper, *J. Am. Chem. Soc.*, 2020, **142**, 11131–11138.

9 (*a*) T. Guntreddi, R. Vanjari and K. N. Singh, *Org. Lett.*, 2014, **16**, 3624–3627; (*b*) W. Cao, F. Dai, R. Hu and B. Z. Tang, *J. Am. Chem. Soc.*, 2020, **142**, 978–986.

10 Y. Cheng, J.-C. Xiang, Z.-X. Wang, J.-T. Ma, M. Wang, B.-C. Tang, Y.-D. Wu, Y.-P. Zhu and A.-X. Wu, *Adv. Synth. Catal.*, 2018, **360**, 550–555.

11 (*a*) H. Huang, Z. Qu, X. Ji and G.-J. Deng, *Org. Chem. Front.*, 2019, **6**, 1146–1150; (*b*) Z. Xu, G. J. Deng, F. Zhang, H. Chen and H. Huang, *Org. Lett.*, 2019, **21**, 8630–8634; (*c*) T. Chivers and P. J. Elder, *Chem. Soc. Rev.*, 2013, **42**, 5996–6005.

12 D. L. Priebbenow and C. Bolm, *Chem. Soc. Rev.*, 2013, **42**, 7870–7880.