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Visible light-induced recyclable g-C_3N_4 catalyzed thiocyanation of C(sp^2)–H bonds in sustainable solvents†‡

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A metal-free photocatalytic strategy for the preparation of thiocyanated heterocycles from inexpensive NH_4SCN has been developed using carbon nitride (g-C_3N_4) as a general heterogeneous catalyst in a green solvent under an air atmosphere and the irradiation of a blue LED. Various thiocyanated heterocycles including indolo[2,1-*a*]isoquinolin-6(5*H*)-ones, benzimidazo[2,1-*a*]isoquinolin-6(5*H*)-ones, thioflavones, azaspiro[4.5]trienones and imidazo[1,2-*a*]pyridines were successfully synthesized in good yields (up to 96%). Importantly, this metal-free and external-oxidant-free procedure employed dimethyl carbonate as a green medium, avoiding the traditional volatile organic solvents. Moreover, the recyclable g-C_3N_4 catalyst could be used at least 8 times without significant loss of activities.

Introduction

In the past decades, the development of clean, economical, and efficient chemical processes has received widespread attention.[1] Visible light, as an easily available and renewable natural resource, has attracted great interest from chemists.[2] In this context, many photocatalytic strategies have been developed to build valuable products in organic synthesis.[3] Among the reported photocatalytic systems, homogeneous photocatalysts like metal complexes and organic dyes are extensively applied.[4] However, these homogeneous catalysts are difficult to recycle and reuse, which may cause environmental issues and high costs. Therefore, the development of efficient heterogeneous catalysts for photocatalytic reactions is highly significant.

In recent years, the application of semiconductor materials as heterogeneous photocatalysts has attracted great interest due to their excellent photovoltaic properties and good stability/recyclability.[5] In particular, graphitic carbon nitride (g-C_3N_4) as an inexpensive, easily available, metal-free, and recyclable semiconductor photocatalyst has emerged as an ideal catalyst for organic synthesis.[6] For example, in 2019, König's group reported the g-C_3N_4 catalyzed bifunctionalization of arenes/heteroarenes under blue light irradiation.[7] In the same year, Hu's group realized visible-light-induced aerobic oxidation of various benzylic C–H bonds with g-C_3N_4 as a catalyst.[8] Recently, our group found that g-C_3N_4 could be an efficient heterogeneous catalyst for the hydroaminomethylation or annulation reaction of quinoxalin-2(1*H*)-ones and *N*-aryl glycines under visible light.[9] Despite these achievements, the application of g-C_3N_4 as a heterogeneous photocatalyst for organic transformations is still in its infancy. Thus, the exploration of novel organic transformations catalyzed by g-C_3N_4 is still highly desirable.

Thiocyanates exhibit various biological activities such as antimicrobial, enzyme inhibitory, and insecticidal in the fields of medicine, pesticides, and materials.[10] Therefore, the installation of a –SCN group into heterocycles has gained huge attention in recent years.[11] For example, Hajra's group used an organic dye (eosin Y) as a photocatalyst to achieve the synthesis of thiocyanated imidazo[1,2-*a*]pyridines under metal-free conditions in 2015.[12] Sarvari's group reported the formation of a C–S bond through direct thiocyanation reactions catalyzed by Alizarin red S-TiO_2 under visible light in 2020.[13] Although great progress has been made, some shortcomings still need to be solved urgently, such as non-recyclable organic dyes and toxic organic solvents. Herein, we disclosed a general photocatalytic thiocyanation protocol using dimethyl carbonate (DMC) as a green solvent (Scheme 1). In this study, with the recyclable g-C_3N_4 as a "universal catalyst", various thiocyanated heterocycles including indolo[2,1-*a*]isoquinolin-6(5*H*)-ones, benzimidazo[2,1-*a*]isoquinolin-6(5*H*)-ones, thioflavones, azaspiro[4.5]trienones and imidazo[1,2-*a*]pyridines were successfully achieved from inexpensive NH_4SCN in good yields. To the best of our knowledge, this is the first case of the construc-

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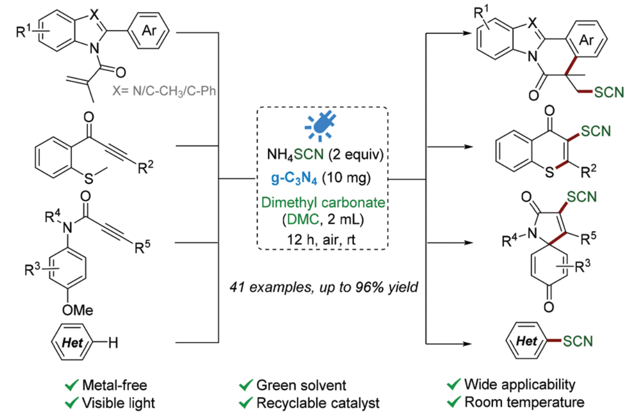


Scheme 1 Synthesis of thiocyanated heterocycles.

tion of thiocyanated indolo/benzimidazo[2,1-a]isoquinolin-6(5*H*)-ones and thioflavones.

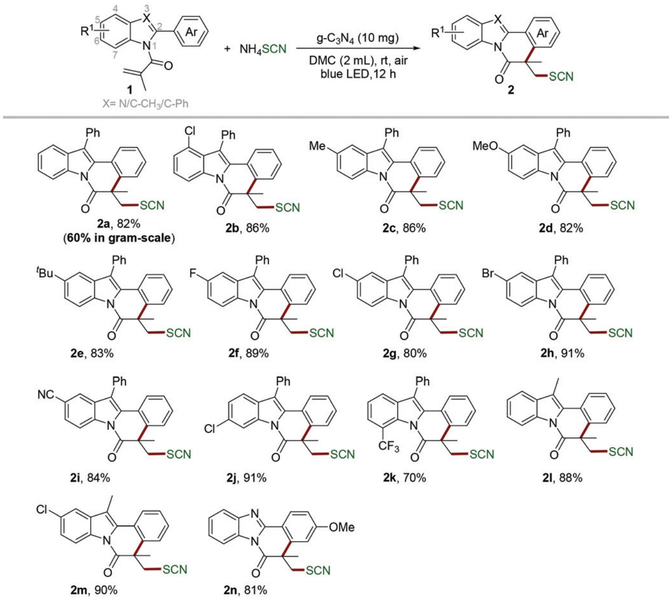
Results and discussion

We initiated our study by establishing optimal experimental conditions using the model reaction of 1-(2,3-diphenyl-1*H*-indol-1-yl)-2-methylprop-2-en-1-one (**1a**) with NH_4SCN in the presence of photocatalysts under the irradiation of a blue LED (for details, see the ESI, Table S1‡). After extensive experiments, the optimal conditions were established as follows: **1a** (0.2 mmol), NH_4SCN (0.4 mmol), g-C_3N_4 (10 mg), DMC (2 mL) at room temperature for 12 h under an air atmosphere and the irradiation of a blue LED.

Subsequently, the substrate scope of this g-C_3N_4 catalyzed reaction was further explored to synthesize various thiocyanated indolo/benzimidazo[2,1-*a*]isoquinoline-6(5*H*)-ones (Table 1). Firstly, the model reaction gave the desired product **2a** in a good isolated yield of 82%. Then the 1-(2,3-diphenyl-1*H*-indol-1-yl)-2-methylprop-2-en-1-ones **1** bearing different substituents R^1 ($-CH_3$, –OMe, –^{t}Bu, –F, –Cl, –Br, –CN and $-CF_3$) were tested (**1b–k**). Initially, the substrate bearing an electron-withdrawing halo group (–Cl) at C4-position gave the desired product **2b** in an excellent yield of 86%. When the substrates with the electron-donating groups ($-CH_3$, –OMe and –^{t}Bu) and electron-withdrawing groups (–F, –Cl, –Br and –CN) were at C5-position, the target products **2c–i** were obtained in good to excellent yields. The 6-Cl, 7-CF_3, and 3-Me substituted substrates also react with NH_4SCN smoothly to give the corresponding products (**2j–m**) in 70–91% yields. Moreover, when the benzimidazole type substrate (**1n**) was employed to react with NH_4SCN, the target product **2n** was obtained in 81% yield. Simultaneously, a gram-scale reaction was performed to synthesize **2a**, and a satisfactory yield of 60% was obtained (Scheme S3‡).

To explore the generality of this thiocyanation strategy, other thiocyanated heterocycles were also synthesized under the optimal reaction conditions. For example, the reaction of methylthiolated alkynones **3** with NH_4SCN under the standard conditions delivered the corresponding thiocyanated thioflavone products **4a–f** in yields of 70–93% (Table 2).

Table 1 Synthesis of thiocyanated indolo/benzimidazo[2,1-a]isoquinolin-6(5*H*)-ones[a]

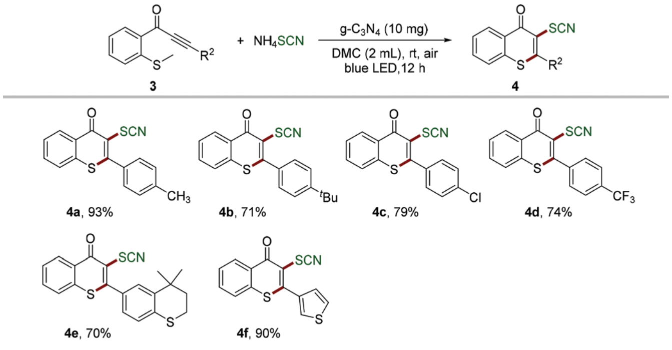


[a] Reaction conditions: **1** (0.2 mmol), NH_4SCN (0.4 mmol), g-C_3N_4 (10 mg) in DMC (2 mL) in air at room temperature for 12 h under the irradiation of a 10 W blue LED. Isolated yields.

Furthermore, the radical cascade reaction of *N*-arylpropiolamide (**5a**) with NH_4SCN under the standard conditions provided the desired 3-thiocyanated azaspiro[4.5]trienone **6a** in 84% yield (Table 3). Further exploration demonstrated that this strategy has a good functional group tolerance, giving various substituted *N*-arylpropiolamides **6b–h** in good yields.

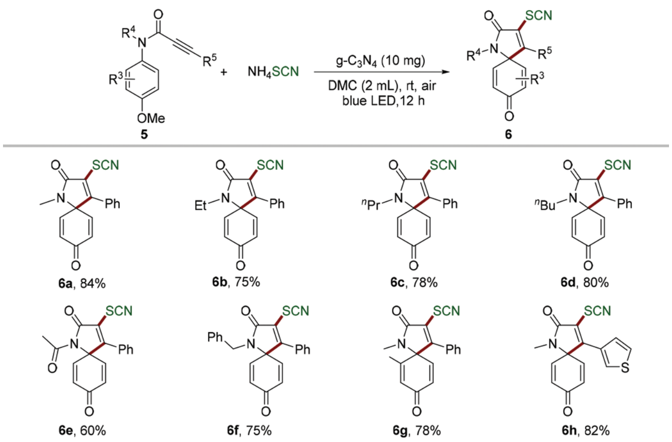
Encouraged by these exciting results, we tried to apply this strategy to the direct thiocyanation of heterocycles (Table 4).

Table 2 Synthesis of thiocyanated thioflavones[a]



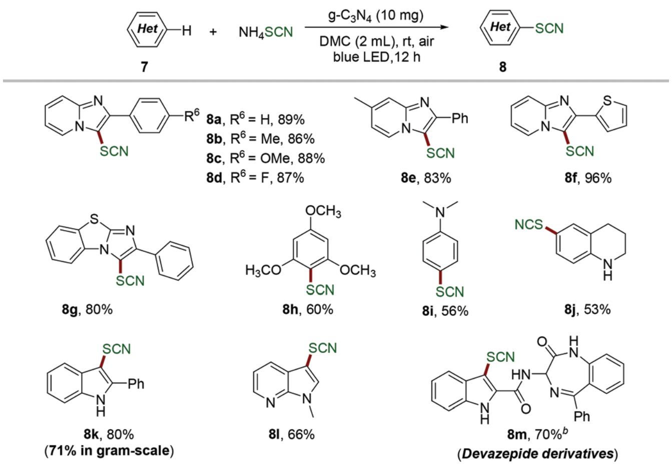
[a] Reaction conditions: **3** (0.2 mmol), NH_4SCN (0.4 mmol), g-C_3N_4 (10 mg) in DMC (2 mL) in air at room temperature for 12 h under the irradiation of a 10 W blue LED. Isolated yields.

Table 3 Synthesis of thiocyanated azaspiro[4.5]trienones[a]



[a] Reaction conditions: **5** (0.2 mmol), NH_4SCN (0.4 mmol), g-C_3N_4 (10 mg) in DMC (2 mL) in air at room temperature for 12 h under the irradiation of a 10 W blue LED. Isolated yields.

Table 4 Synthesis of thiocyanated heterocycles[a]



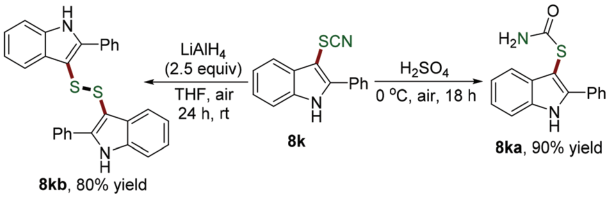
[a] Reaction conditions: **7** (0.2 mmol), NH_4SCN (0.4 mmol), g-C_3N_4 (10 mg) in DMC (2 mL) in air at room temperature for 12 h under the irradiation of a 10 W blue LED. Isolated yields. [b] Reaction for 76 h.

First, the reaction of different substituted 2-aryl imidazo[1,2-a] pyridines and NH_4SCN were conducted under the standard conditions. It was gratifying that the corresponding target products **8a–f** were obtained in excellent yields (83–96%). Notably, 2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazole could also be used in this strategy to produce the target compound **8g** in 80% yield. Moreover, other heterocycles including 1,3,5-trimethoxybenzene, *N*,*N*-dimethylaniline, tetrahydroquinoline, 2-phenylindole, and azaindole were all applicable in this protocol to react with NH_4SCN under the standard conditions, giving the corresponding products **8h–l** in moderate to excellent yields. Surprisingly, thiocyanation of the popular drug cholecystokinin antagonist devazepide derivative **8m** could also be achieved in 70% yield, albeit a long reaction time was required.[14] Meanwhile, an isolated yield of 71% was obtained in the gram-scale synthesis of **8k** (Scheme S3‡), suggesting that the catalytic procedure is practically promising.

To explore the synthetic application of thiocyanated heterocycles, the synthesized compound **8k** was treated with sulfuric acid and $LiAlH_4$. As shown in Scheme 2, the thioamide compound **8ka** and the indole sulfide **8kb** were obtained in good yields.

We further carried out the recovery experiments of g-C_3N_4 to verify the stability and reusability of the catalytic system. Under the standard conditions, the model reaction of **1a** and NH_4SCN gave 82% of product **2a**. Then the catalyst g-C_3N_4 was recycled by centrifugation, and washed twice with water and ethanol, respectively, and then dried at 80 °C. Next, the recovered g-C_3N_4 was used in the next run. As shown in Fig. 1i, the catalytic activity of the recovered g-C_3N_4 almost remained constant in the 8th run. After that, powder X-ray diffraction (XRD) was used to characterize the fresh g-C_3N_4 and recovered g-C_3N_4 after the reaction. As shown in Fig. 1ii, the structure of the recovered g-C_3N_4 still did not change compared with the fresh g-C_3N_4,[15] which was further confirmed by the scanning electron microscopy (SEM) and the transmission electron microscopy (TEM) images (Fig. 2). These results suggested that g-C_3N_4 is a stable heterogeneous photocatalyst in this reaction.[16]

Subsequently, the sensitivity of this strategy was evaluated based on the reaction conditions, which will help us to strengthen the understanding of this new synthetic method and its reproducibility, following the protocol reported by Glorius *et al.* (Table 5).[17] The results were shown in the radar diagram, from which we could quickly assess the sensitivity of this strategy. It can be seen from the radar diagram that the light intensity is a key parameter affecting the strategy, while



Scheme 2 Synthetic transformations of **8k**.

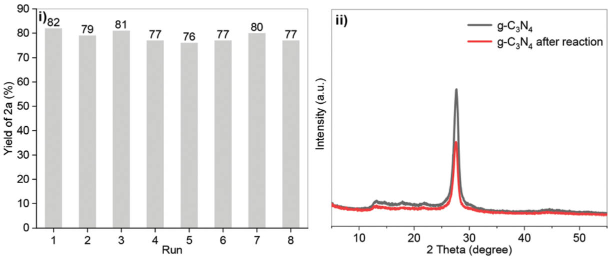


Fig. 1 (i) Recyclability of the catalyst and (ii) the XRD pattern of the catalyst.

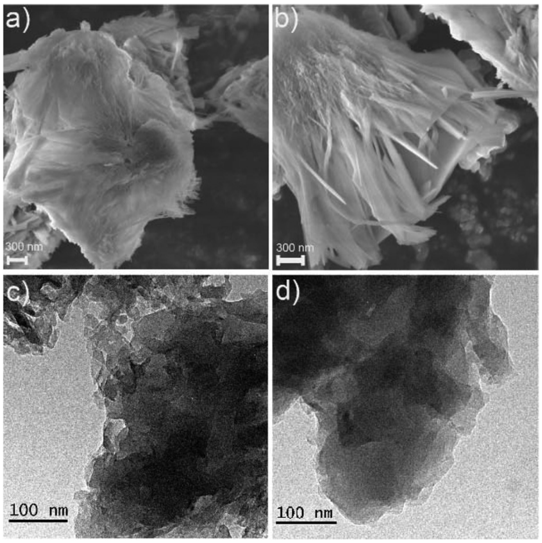
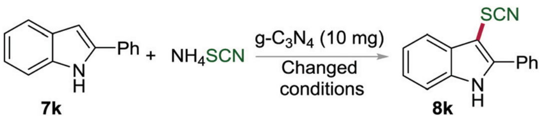
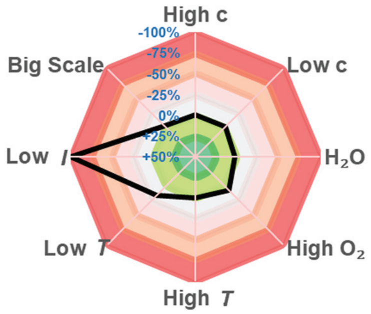


Fig. 2 (a) SEM image of the fresh g-C_3N_4; (b) SEM image of the recovered g-C_3N_4; (c) TEM image of the fresh g-C_3N_4; and (d) TEM image of the recovered g-C_3N_4.

Table 5 Sensitivity assessment of this reaction



Variation of parameters	Lower point	Center point	Higher point
Concentration (c)	$c - 10\%\ c$	Standard conditions	$c + 10\%\ c$
H_2O level			$+H_2O$; $V_{H2O} = 1\%\ V_{rxn}$
O_2 level			Air
Temperature (T)	$T - 10$ °C		$T + 10$ °C
Light intensity (I)	$I/20$		
Scale			n*25
∑Reactions	3		5

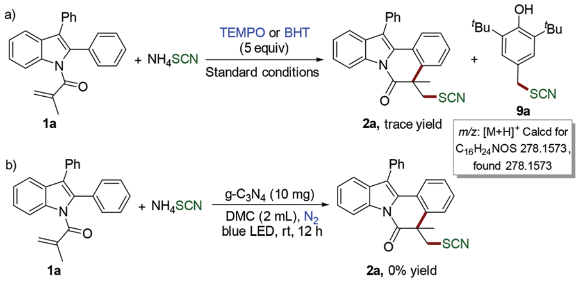


the other parameters have almost no effect on the reaction and can be regarded as random errors. On the other hand, these results also demonstrated the good tolerance of this strategy.

After that, we further explored the reaction mechanism through control experiments, as shown in Scheme 3. When the radical scavengers 2,2,6,6-tetramethylpiperidin-1-yl-oxyalkyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) were added to the reaction mixtures, the thiocyanation reactions were completely suppressed (Scheme 3a). The signal appearing at *m*/*z* 278.1573 of the high-resolution mass spectra (HRMS) indicated that the adduct **9a** was formed, suggesting that the SCN radical was generated in the reaction (Fig. S2‡). Moreover, the reaction under N_2 did not afford the desired product, indicating that O_2 played an indispensable role in this transformation (Scheme 3b).

In addition, the electron paramagnetic resonance (EPR) experiments were performed under blue light irradiation (Fig. 3). When the radical spin trapping reagent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was added to the NH_4SCN solution under the standard conditions, a signal was observed. We speculated that the radical might be generated under the promotion of visible light. (Fig. 3, and for details, see the ESI, Fig. S4‡).

According to the experimental results and previous reports, a tentative mechanism was proposed for this visible-light promoted reaction, which was catalyzed by g-C_3N_4 (Scheme 4). First, under the irradiation of visible light, g-C_3N_4 absorbs photons and generates holes in the valence band (VB) and electrons in the conduction band (CB). Then, the holes generated by the VB (E_{VB} = + 1.2 V *vs.* SCE)[7] obtain the electrons from NH_4SCN (Fig. S3,‡ $E_{1/2}{}^{ox}$ = + 0.60 V *vs.* SCE was measured) *via* a single electron transfer (SET) to generate the SCN radical. Simultaneously, the electrons in the CB were transferred to O_2 (air) through a SET to generate $O_2{\cdot}^-$. Then, the SCN radical was added to the C=C bonds of **1a** to generate the radical intermediate **9b**, which was then subjected to an intra-



Scheme 3 Control experiments.

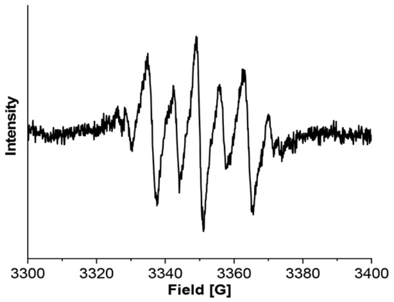
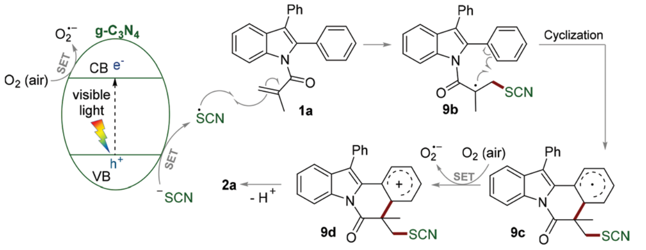


Fig. 3 EPR spectrum of a mixture of DMPO and NH_4SCN under the irradiation of a blue LED.



Scheme 4 Plausible mechanism.

molecular cyclization to obtain the radical intermediate **9c**. Furthermore, **9c** was oxidized by O_2 (air) to form the carbocation **9d** through a SET process. Then **9d** was finally transformed into the target product **2a** by deprotonation.

Conclusions

In summary, we have developed a simple, efficient, green, and sustainable visible light-promoted heterogeneous g-C_3N_4 catalyzed synthetic strategy to construct thiocyanated indolo/benzimidazo[2,1-*a*]isoquinolin-6(5*H*)-ones, thioflavones and other heterocyclic compounds using low-cost and easily available NH_4SCN as a raw material. This general method showed the advantages such as having a metal-free procedure and an external-oxidant-free procedure, utilizing a recyclable catalyst and a green solvent, having a wide applicability, being able to be applied at room temperature, and being easy to scale up. The application of g-C_3N_4 in the field of green organic synthesis is under exploration in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 (*a*) J. Jiang, F. Xiao, W.-M. He and L. Wang, *Chin. Chem. Lett.*, 2021, DOI: 10.1016/j.cclet.2021.02.057; (*b*) X. He, L.-Q. Qiu, W.-J. Wang, K.-H. Chen and L.-N. He, *Green Chem.*, 2020, **22**, 7301–7320; (*c*) Z. Chen, S. Du, J. Zhang and X.-F. Wu, *Green Chem.*, 2020, **22**, 8169–8182; (*d*) P. Mao, J. Zhu, J. Yuan, L. Yang, Y. Xiao and C. Zhang, *Chin. J. Org. Chem.*, 2019, **39**, 1529–1547.

2 (*a*) Z. Gan, G. Li, X. Yang, Q. Yan, G. Xu, G. Li, Y.-Y. Jiang and D. Yang, *Sci. China: Chem.*, 2020, **63**, 1652–1658; (*b*) Z. Gan, G. Li, Q. Yan, W. Deng, Y.-Y. Jiang and D. Yang, *Green Chem.*, 2020, **22**, 2956–2962; (*c*) Q. Yu, Y. Zhang and J.-P. Wan, *Green Chem.*, 2019, **21**, 3436–3441; (*d*) J. Gao, J. Feng and D. Du, *Chem. – Asian J.*, 2020, **15**, 3637–3659; (*e*) X.-Y. Yu, J.-R. Chen and W.-J. Xiao, *Chem. Rev.*, 2021, **121**, 506–561; (*f*) X. Yuan, G. Yang and B. Yu, *Chin. J. Org. Chem.*, 2020, **40**, 3620–3632.

3 (*a*) N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166; (*b*) K. L. Skubi, T. R. Blum and T. P. Yoon, *Chem. Rev.*, 2016, **116**, 10035–10074; (*c*) Y. Chen, L.-Q. Lu, D.-G. Yu, C.-J. Zhu and W.-J. Xiao, *Sci. China: Chem.*, 2019, **62**, 24–57; (*d*) K. Sun, Q.-Y. Lv, X.-L. Chen, L.-B. Qu and B. Yu, *Green Chem.*, 2021, **23**, 232–248; (*e*) Y.-Q. Jiang, J. Li, Z.-W. Feng, G.-Q. Xu, X. Shi, Q.-J. Ding, W. Li, C.-H. Ma and B. Yu, *Adv. Synth. Catal.*, 2020, **362**, 2609–2614; (*f*) J. Shi and W. Wei, *Chin. J. Org. Chem.*, 2020, **40**, 2170–2172; (*g*) C. Raviola, S. Protti, D. Ravelli and M. Fagnoni, *Green Chem.*, 2019, **21**, 748–764.

4 (*a*) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363; (*b*) W.-M. Cheng and R. Shang, *ACS Catal.*, 2020, **10**, 9170–9196; (*c*) T. Y. Shang, L. H. Lu, Z. Cao, Y. Liu, W. M. He and B. Yu, *Chem. Commun.*, 2019, **55**, 5408–5419; (*d*) B.-G. Cai, J. Xuan and W.-J. Xiao, *Sci. Bull.*, 2019, **64**, 337–350; (*e*) J. Zhu, W. C. Yang, X. D. Wang and L. Wu, *Adv. Synth. Catal.*, 2018, **360**, 386–400; (*f*) A. Vega-Peñaloza, J. Mateos, X. Companyó, M. Escudero-Casao and L. Dell'Amico, *Angew. Chem., Int. Ed.*, 2021, **60**, 1082–1097.

5 (*a*) X. Zhu, Y. Lin, J. San Martin, Y. Sun, D. Zhu and Y. Yan, *Nat. Commun.*, 2019, **10**, 2843; (*b*) Y. Yuan, H. Zhu, K. Hills-Kimball, T. Cai, W. Shi, Z. Wei, H. Yang, Y. Candler, P. Wang, J. He and O. Chen, *Angew. Chem., Int. Ed.*, 2020, **59**, 22563–22569; (*c*) T. Shi, K. Sun, X.-L. Chen, Z.-X. Zhang, X.-Q. Huang, Y.-Y. Peng, L.-B. Qu and B. Yu, *Adv. Synth. Catal.*, 2020, **362**, 2143–2149; (*d*) X.-B. Li, Z.-K. Xin, S.-G. Xia, X.-Y. Gao, C.-H. Tung and L.-Z. Wu, *Chem. Soc. Rev.*, 2020, **49**, 9028–9056.

6 (*a*) K. S. Lakhi, D. H. Park, K. Al-Bahily, W. Cha, B. Viswanathan, J. H. Choy and A. Vinu, *Chem. Soc. Rev.*, 2017, **46**, 72–101; (*b*) J. Guo, Y. Wang, Y. Li, K. Lu, S. Liu, W. Wang and Y. Zhang, *Adv. Synth. Catal.*, 2020, **362**, 3898–3904; (*c*) Y. Markushyna, C. A. Smith and A. Savateev, *Eur. J. Org. Chem.*, 2020, 1294–1309; (*d*) J. Wang, B. Ni, T. Niu and F. Ji, *Catal. Sci. Technol.*, 2020, **10**, 8458–8464; (*e*) A. Savateev, I. Ghosh, B. König and M. Antonietti, *Angew. Chem., Int. Ed.*, 2018, **57**, 15936–15947; (*f*) J.-Q. Di, M. Zhang, Y.-X. Chen, J.-X. Wang, S.-S. Geng, J.-Q. Tang and Z.-H. Zhang, *Green Chem.*, 2021, **23**, 1041–1049; (*g*) S.-J. Chen, T.-F. Niu and B.-Q. Ni, *Chin. J. Synth. Chem.*, 2021, DOI: 10.15952/j.cnki.cjsc.1005-1511.20001; (*h*) T. Niu, S. Chen, M. Hong, T. Zhang, J. Chen, X. Dong and B. Ni,

Green Chem., 2020, **22**, 5042–5049; (*i*) B. Ni, B. Zhang, J. Han, B. Peng, Y. Shan and T. Niu, *Org. Lett.*, 2020, **22**, 670–674.

7 I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti and B. König, *Science*, 2019, **365**, 360–366.

8 P. Geng, Y. Tang, G. Pan, W. Wang, J. Hu and Y. Cai, *Green Chem.*, 2019, **21**, 6116–6122.

9 Y.-F. Si, X.-L. Chen, X.-Y. Fu, K. Sun, X. Song, L.-B. Qu and B. Yu, *ACS Sustainable Chem. Eng.*, 2020, **8**, 10740–10746.

10 (*a*) E. Elhalem, B. N. Bailey, R. Docampo, I. Ujváry, S. H. Szajnman and J. B. Rodriguez, *J. Med. Chem.*, 2002, **45**, 3984–3999; (*b*) R. J. Capon, C. Skene, E. H.-T. Liu, E. Lacey, J. H. Gill, K. Heiland and T. Friedel, *J. Org. Chem.*, 2001, **66**, 7765–7769; (*c*) Yasman, R. A. Edrada, V. Wray and P. Proksch, *J. Nat. Prod.*, 2003, **66**, 1512–1514; (*d*) Q. Chen, Y. Lei, Y. Wang, C. Wang, Y. Wang, Z. Xu, H. Wang and R. Wang, *Org. Chem. Front.*, 2017, **4**, 369–372; (*e*) Q. Xu, L. Zhang, G. Feng and C. Jin, *Chin. J. Org. Chem.*, 2019, **39**, 287–300; (*f*) G. Jiang, C. Zhu, J. Li, W. Wu and H. Jiang, *Adv. Synth. Catal.*, 2017, **359**, 1208–1212.

11 (*a*) T. Castanheiro, J. Suffert, M. Donnard and M. Gulea, *Chem. Soc. Rev.*, 2016, **45**, 494–505; (*b*) L. Zhang, C. Niu, X. Yang, H. Qin, J. Yang, J. Wen and H. Wang, *Chin. J. Org. Chem.*, 2020, **40**, 1117–1128; (*c*) Y.-J. Chen, Y.-H. He and Z. Guan, *Tetrahedron*, 2019, **75**, 3053–3061; (*d*) L.-N. Guo, Y.-R. Gu, H. Yang and J. Hu, *Org. Biomol. Chem.*, 2016, **14**, 3098–3104; (*e*) A. Dey and A. Hajra, *Adv. Synth. Catal.*, 2019, **361**, 842–849; (*f*) P.-F. Yuan, Q.-B. Zhang, X.-L. Jin, W.-L. Lei, L.-Z. Wu and Q. Liu, *Green Chem.*, 2018, **20**, 5464–5468; (*g*) D. Zhang, H. Wang and C. Bolm, *Chem. Commun.*, 2018, **54**, 5772–5775; (*h*) Y. Gao, Y. Liu and J.-P. Wan, *J. Org. Chem.*, 2019, **84**, 2243–2251; (*i*) W. Fan, Q. Yang, F. Xu and P. Li, *J. Org. Chem.*, 2014, **79**, 10588–10592; (*j*) F. Lu, K. Zhang, Y. Yao, Y. Yin, J. Chen, X. Zhang, Y. Wang, L. Lu, Z. Gao and A. Lei, *Green Chem.*, 2021, **23**, 763–766.

12 S. Mitra, M. Ghosh, S. Mishra and A. Hajra, *J. Org. Chem.*, 2015, **80**, 8275–8281.

13 M. Koohgard, Z. Hosseinpour, A. M. Sarvestani and M. Hosseini-Sarvari, *Catal. Sci. Technol.*, 2020, **10**, 1401–1407.

14 R. Herranz, *Med. Res. Rev.*, 2003, **23**, 559–605.

15 M. H. Muhammad, X.-L. Chen, Y. Liu, T. Shi, Y. Peng, L. Qu and B. Yu, *ACS Sustainable Chem. Eng.*, 2020, **8**, 2682–2687.

16 S. Zhang, W. Yi, Y. Guo, R. Ai, Z. Yuan, B. Yang and J. Wang, *Nanoscale*, 2021, **13**, 3493–3499.

17 (*a*) L. Pitzer, F. Schäfers and F. Glorius, *Angew. Chem., Int. Ed.*, 2019, **58**, 8572–8576; (*b*) F. Gao, K. Sun, X.-L. Chen, T. Shi, X.-Y. Li, L.-B. Qu, Y.-F. Zhao and B. Yu, *J. Org. Chem.*, 2020, **85**, 14744–14752.