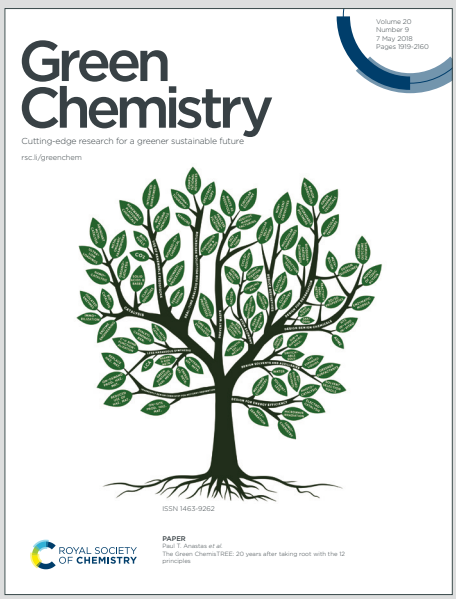
View Article Online
View Journal

Green Chemistry

Cutting-edge research for a greener sustainable future

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. Ran, L. Song, Y. Niu, M. Wei, Z. Zhang, X. Zhou and D. Yu, *Green Chem.*, 2021, DOI: 10.1039/D0GC03723K.



View Article Online
DOI: 10.1039/D0GC03723K

COMMUNICATION

Transition-metal-free synthesis of thiazolidin-2-ones and 1,3-thiazinan-2-ones from arylamines, elemental sulfur and CO_2

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Chuan-Kun Ran,[a] Lei Song,[a] Ya-Nan Niu,[a] Ming-Kai Wei,[a] Zhen Zhang,*[b] Xiao-Yu Zhou[a] and Da-Gang Yu*[a]

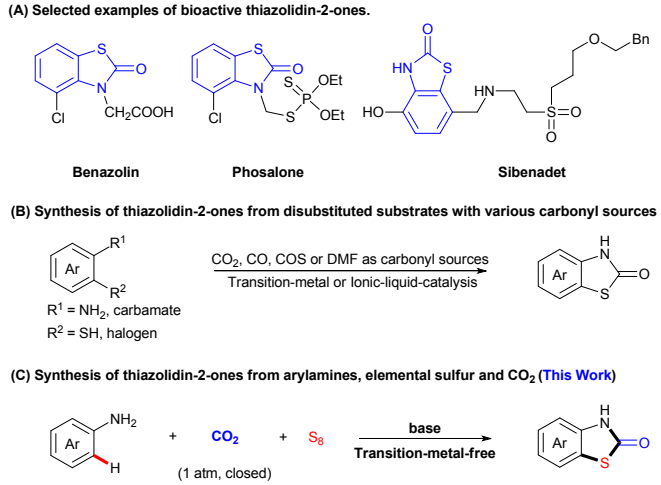
Transfering waste to treasure is highly important in green chemistry. However, it is difficult to realize it efficiently due to the low reactivity, especially the simultaneous utilization of two unreactive feedstocks in one reaction. Herein, we report the first utilization of both elemental sulfur and CO_2 in a multi-component reaction to generate valuable thiazolidin-2-ones and 1,3-thiazinan-2-ones. Under transition-metal-free reaction conditions, a variety of easily available arylamines react with elemental sulfur and CO_2 (1 atm) to give functional thiazolidin-2-ones and 1,3-thiazinan-2-ones in moderate to good yields via C–H bond functionalization. This strategy is highlighted by high step economy with generation of three bonds in one reaction and good functional groups tolerance.

Tremendous efforts have been devoted to the development of green and sustainable chemistry, given the significance of its environmental impact and sustainability both in academia and industry. Among diverse investigation, the formation of valuable chemicals using CO_2 as the C1 source is an attractive strategy due to the abundance, availability, sustainability, and nontoxicity of CO_2.[1] Although the thermodynamic stability and kinetic inertness of CO_2 set challenges for its utilization in organic synthesis, many kinds of CO_2 transformations have been developed to construct important carbonyl-containing heterocycles.[2] Recently, carbonylation of C–H bonds with CO_2 has emerged as an efficient and highly promising strategy to generate a variety of valuable carbonyl-containing heterocycles base on the concept of "CO_2 = CO + [O]".[3,4] It is still highly desirable to develop other sustainable strategies for the construction of carbonyl-containing heterocycles via C–H functionalization.

Thiazolidin-2-ones are important structural motifs in a large number of pharmaceuticals, agrochemicals, and natural products (Scheme 1A).[5] Therefore, the development of efficient protocols for selective synthesis of thiazolidin-2-one derivatives is of much interest and importance. Recently, many groups have made great contributions to this field by developing various strategies to generate thiazolidin-2-ones with a series of carbonyl sources (e.g., CO_2, CO, COS, or DMF).[6] In most cases, however, the substrates are limited to bifunctional arenes bearing two functional groups (e.g., halogen, sulfur-containing groups) (Scheme 1B).[7] To the best of our knowledge, the mono-functionalized substrates, such as arylamines, have not been used to construct thiazolidin-2-ones with CO_2 and one sulfur source. Considering that elemental sulfur (S_8), which is non-toxic, stable, inexpensive and easy to handle, is well known as industrial waste[8] and has been applied in C–S bond formation,[9] we hypothesized whether we could construct thiazolidin-2-one derivatives by using three simple and easily available substrates, including aryl amines, S_8 and CO_2. However, there are several challenges. First of all, the formation of C–S bond via C–H bond sulfuration is inefficient due to the low activity of C–H bonds and S_8. Moreover, the inert property of CO_2 might also hamper the carbonylation. Thus, the low reactivities of such three components might call for harsh reaction conditions, which would cause problems to control the chemo- and regio-selectivities. For example, di- or multi-sulfuration instead of mono-sulfuration might happen. The generation of other carbonylative products, such as ureas and carbamates, is also possible. Therefore, it is highly challenging to develop an efficient and selective three-component reaction to directly synthesize thiazolidin-2-ones by using two unreactive feedstocks. With our continuous interest in the utilization of CO_2 to generate carbonyl-containing heterocycles, herein we report a practical three-component reaction to generate valuable thiazolidin-2-ones from arylamines, S_8, and CO_2 (1 atm) under transition-metal-free and redox-neutral conditions (Scheme 1C).

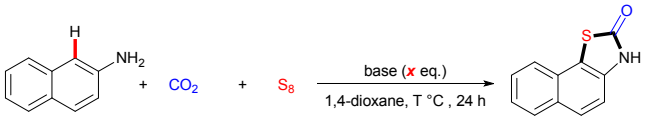
[a] Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China. Email: dgyu@scu.edu.cn
[b] Key laboratory of Coarse Cereal Processing of Ministry of Agriculture and Rural Affairs, College of Pharmacy and Biological Engineering, Chengdu University, Chendu 610106, P. R. China. Email: zhangzhen1@cdu.edu.cn
†Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

View Article Online DOI: 10.1039/D0GC03723K



Scheme 1 Importance and synthesis of thiazolidin-2-ones.

Table 1 Optimization of reaction conditions[a]

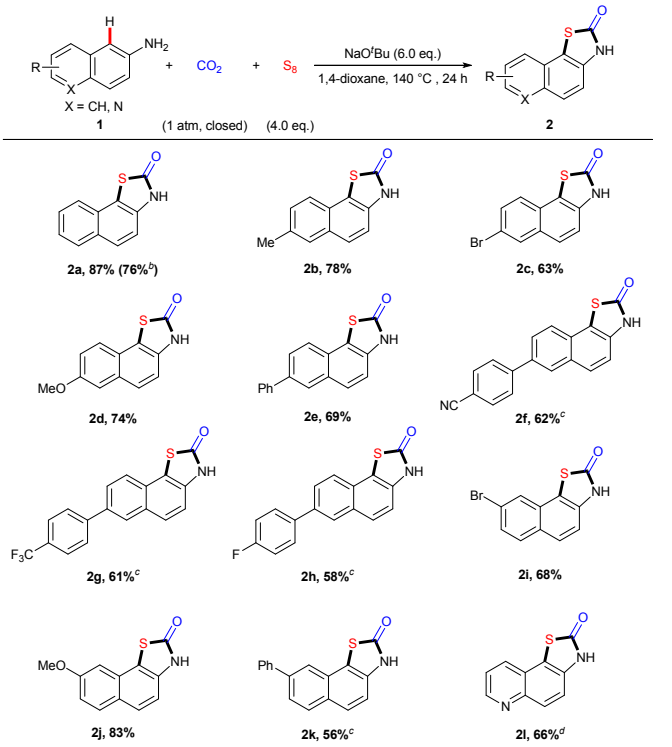


entry	base	x	T /°C	yield (%)[b]	entry	base	x	T /°C	yield (%)[b]
1	LiO^{t}Bu	5	140	44	10[c]	NaO^{t}Bu	6	140	35
2	KO^{t}Bu	5	140	62	11[d]	NaO^{t}Bu	6	140	74
3	NaO^{t}Bu	5	140	78	12[e]	NaO^{t}Bu	6	140	22
4	Cs_2CO_3	5	140	8	13[f]	NaO^{t}Bu	6	140	35
5	NaO^{t}Bu	3	140	24	14[g]	NaO^{t}Bu	6	140	12
6	NaO^{t}Bu	4	140	40	15[h]	NaO^{t}Bu	6	140	36
7	**NaO^{t}Bu**	**6**	**140**	**87**	16[i]	NaO^{t}Bu	6	140	68
8	NaO^{t}Bu	6	120	n.d.	17[j]	NaO^{t}Bu	6	140	n.d.
9	NaO^{t}Bu	6	130	34	18[k]	NaO^{t}Bu	6	140	n.d.

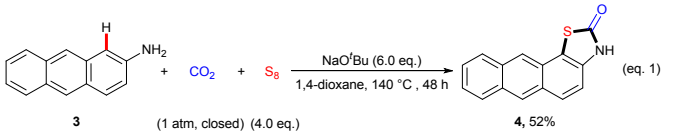
[a]Reaction Conditions: **1a** (0.2 mmol), S_8 (32 g/mol, 0.8 mmol, 25.6 mg), CO_2 (1 atm, closed), 1,4-dioxane (1 mL), 24 h. [b]Isolated yields. [c]S_8 (32 g/mol, 0.4 mmol, 12.8 mg). [d]S_8 (32 g/mol, 0.6 mmol, 19.2 mg). [e]diglyme (1.0 mL). [f]*N*,*N*-Dimethylformamide (DMF, 1.0 mL). [g]*N*,*N*-Dimethylacetamide (DMA, 1.0 mL). [h]Dimethyl sulfoxide (DMSO, 1.0 mL). [i]1,4-Dioxane (2.0 mL). [j]Without S_8. [k]Under the atmospheric of N_2 instead of CO_2. n.d. = not detected.

We began to investigate the reaction using naphthalen-2-amine **1a** as the standard substrate with S_8 as the sulfur source under one atmosphere of CO_2 (Table 1). To our delight, the desired product **2a** was obtained in 78% yield with NaO^{t}Bu as base and 1,4-dioxane as solvent at 140 °C for 24 h (Table 1, entry 3). This reaction is highly regioselective, as the sulfuration at the C3-position was not detected. A variety of bases, such as LiO^{t}Bu, KO^{t}Bu, and Cs_2CO_3, were tested to give lower yields than NaO^{t}Bu (Table 1, entries 1-4). The screening of the amount of NaO^{t}Bu demonstrated that 6.0 equivalent was the best choice (Table 1, entries 5-7). Moreover, lowering reaction temperature also provided worse results, which might arise from the unfavorable carbonylation and sulfuration with unreactive CO_2 and S_8 (Table 1, entries 8-9). Furthermore, we also examined the amount of S_8 and found that 4.0 equivalent of S_8 was the best choice (Table 1, entries 10-11). Other solvents, such as diglyme, DMF, DMA, and DMSO, were also tested and gave poor results (Table 1, entries 12-15), indicating a unique role of 1,4-dioxane in this reaction. Further change in concentration did not improve the reaction (Table 1, entry 16). Control experiments showed that both CO_2 and S_8 were vital to this transformation (Table 1, entries 17-18).

Table 2. Substrate scope of naphthalen-2-amines and quinolin-6-amine[a]



[a]Reaction conditions: **1** (0.2 mmol), S_8 (32 g/mol, 0.8 mmol, 25.6 mg), NaO^{t}Bu (6.0 eq.), CO_2 (1 atm, closed), 1,4-dioxane (1 mL), 24 h, 140 °C. Isolated yields. [b]Gram scale. [c]48 h. [d]72 h

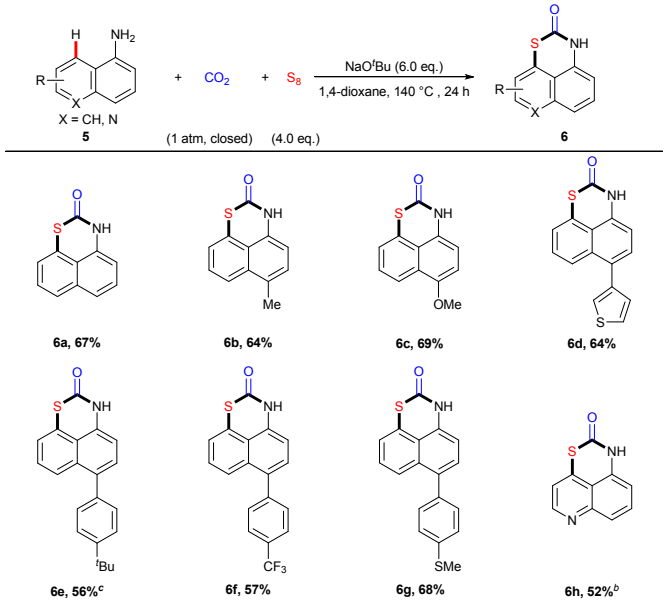


With the optimal reaction conditions in hand, we explored the substrate scope and generality of the three-component reaction (Table 2). We found that diverse naphthalen-2-amines **1a**-**k** underwent this transformation smoothly to afford the expected products in 56%-87% yields. Notably, a gram-scale reaction of **1a** (8 mmol), CO_2, and S_8 was successfully performed to give **2a** in 76% yield. Different substituents, such as electron-neutral groups, electron-donating groups (EDGs) and electron-withdrawing groups (EWGs), did not affect the reaction. Various functional groups, such as methoxyl, trifluoromethyl, cyano groups, C-Br and C-F bonds, were tolerated well. Importantly, the quinolin-6-amine **1l** also showed good reactivity in this transformation. Moreover, a

related fused aryl amine, anthracen-2-amine **3**, could also take part in this transformation to generate the desired product **4** in moderate yield (eq. 1).

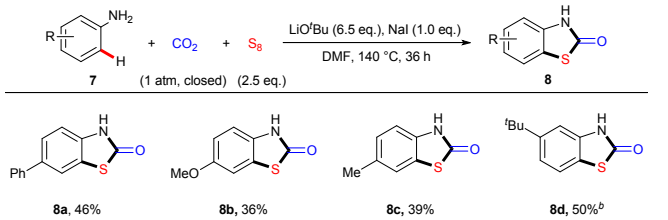
In addition to naphthalen-2-amines, the reactions of naphthalen-1-amines **5** could also proceed well, furnishing the target products with moderate to good yields (Table 3). Interestingly, the sulfuration of **5** happened selectively at the C8-position to construct 1,3-thiazinan-2-ones with the 6-member ring. A variety of naphthalen-1-amines **5** bearing different substituents, such as methoxyl, thiophene, thiol, and trifluoromethyl group, could undergo this transformation to provide the desired products in good yields. Similarly, the quinolin-5-amine **5h** also behaved well in this transformation.

Table 3. Substrate scope of naphthalen-1-amines and quinolin-5-amine[a]



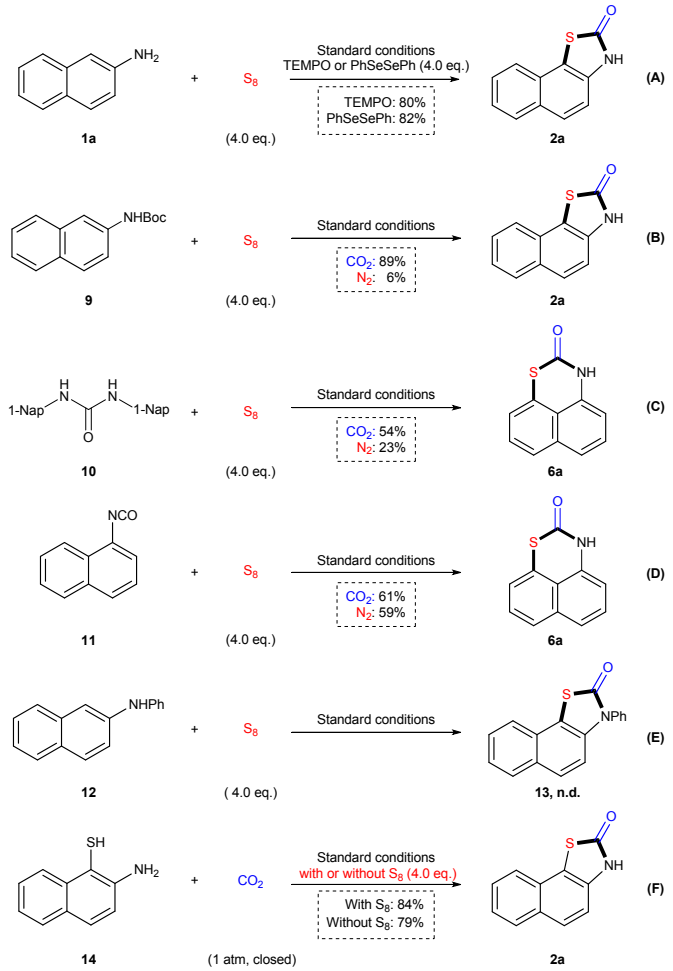
[a]Reaction conditions: **5** (0.2 mmol), S_8 (32 g/mol, 0.8 mmol, 25.6 mg), NaO^{t}Bu (6.0 eq.), CO_2 (1 atm, closed), 1,4-dioxane (1 mL), 24 h, 140 °C. Isolated yields. [b]72 h

Table 4. Substrate scope of anilines[a]



[a]Reaction conditions: **7** (0.2 mmol), S_8 (32 g/mmol, 0.5 mmol, 16 mg), LiO^{t}Bu (6.5 eq.), NaI (1.0 eq.), CO_2 (1 atm, closed), DMF (0.5 mL), 36 h, 140 °C. Isolated yields. [b]60 h.

To demonstrate the power of the strategy, we further challenged us by testing less reactive anilines in this reaction, which would be even more difficult arising from a higher energy barrier for the possible dearomization process in the sulfuration step. To our delight, after slightly modifying the reaction conditions with additional NaI, which might make the isocyanate intermediate more active[10] and/or promote the S–S bond cleavage, we could apply simple anilines **7** in such a three-component reaction to give the desired products **8a-8d** in moderate yields (Table 4). When we used a *meta*-substituted aniline **7d** as the substrate, we observed a highly regioselective sulfuration at the position with less steric hindrance. As the *ortho*-substituted anilines are less reactive due to the steric hindrance, the corresponding products could only be obtained with low yields (Please see Supporting Information (SI) for details). Successful implementation of these reactions suggests that this strategy would be useful for the formation of valuable thiazolidin-2-one derivatives.

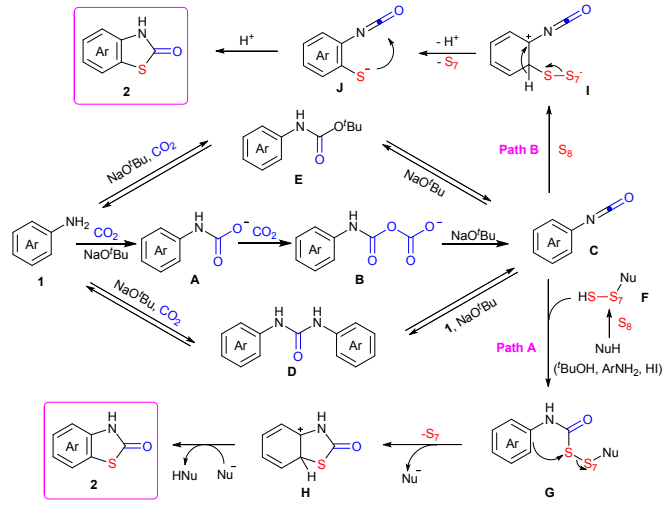


Scheme 2 Control experiments. 1-Nap = 1-naphthyl

To shed light on the mechanism of this reaction, a variety of control experiments were performed (Scheme 2). In the presence of TEMPO or PhSeSePh as the radical scavenger (Scheme 2A), the reaction of **1a** underwent smoothly to give the desired product **2a** in 80% and 82% yield respectively, which implied that a single electron transfer pathway might not be involved in this reaction. As we could detect the carbamate and urea as by-products in the reaction mixture, we applied *tert*-butyl naphthalen-2-ylcarbamate **9**, 1,3-di(naphthalen-1-yl)urea **10** and 1-isocyanatonaphthalene **11** as starting materials in such a transformation respectively (Scheme 2B-D). We found all of these three compounds could be transformed into the final products under CO_2 or N_2 atmosphere.

However, the efficiency of the reactions of **9** and **10** under N_2 was much lower than those under CO_2, indicating that neither carbamate nor urea is the key intermediate to undergo following sulfuration. Moreover, *N*-phenylnaphthalen-2-amine **12** could not be converted into **13** under the standard conditions (Scheme 2E). All of these results indicated that the isocyanate might be the most active intermediate to generate the desired product. When we applied 2-aminonaphthalene-1-thiol **14** in the reaction in the presence or absence of S_8, we could obtain the desired product **2a** in good yields in both cases (Scheme 2F). However, we were not able to detect the sulfuration of arylamines under standard reaction conditions, which indicated that the sequence of sulfuration and then carbonylation might be less favored. Therefore, we speculate that the formation of isocyanate and following cyclization reaction would be more favored to provide the desired product.

Based on the results above and previous reports,[4e,4p,10] we proposed a possible mechanism (Scheme 3). Arylamine **1** might react with two molecules of CO_2 in the presence of NaO^{t}Bu to generate the isocyanate **C**, along with the formation of **A** and **B** as intermediates as well as $NaHCO_3$ and HO^{t}Bu as by-products.[4p] Both of **D** and **E**, which might be formed from **1** or **C** in the presence of CO_2 and/or NaO^{t}Bu, could also decompose to generate **1** and **C**. Meanwhile, nucleophilic attack to elemental sulfur might lead to ring-opening generation of **F**.[9l] Then, nucleophilic attack of **F** to the isocyanate **C** would generate **G** (Path A), which could further undergo intramolecular sulfuration to give **H**. Final deprotonation and re-aromatization would afford the desired product. The intermolecular sulfuration of arylamine derivatives, such as **1** and intermediates **A**-**E**, with S_8 to generate the aryl thiolate **J** (Path B) and following intramolecular cyclization with isocyanates might also be possible (Please see SI for details).



Scheme 3. Proposed Mechanism

Conclusions

In summary, we have developed the first three-component reaction to synthesize valuable thiazolidin-2-ones from arylamines, S_8, and CO_2 via C(sp^2)–H bond functionalization. This strategy features easy availability of starting materials, broad substrate scope, and good functional group tolerance, allowing access to a series of functionalized thiazolidin-2-one derivatives in the absence of transition metals and external oxidants. The preliminary mechanistic studies indicate that isocyanate might be the key intermediate.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the National Natural Science Foundation of China (21822108, 21801025), Sichuan Science and Technology Program (2019YJ0669, 20CXTD0112), and the Fundamental Research Funds for the Central Universities for financial support. We also thank the comprehensive training platform of the Specialized Laboratory in the College of Chemistry at Sichuan University for compound testing.

Notes and references

1 (a) M. Aresta, Ed. *Carbon Dioxide as Chemical Feedstock*; Wiley-VCH: Weinheim, Germany, 2010; (b) L.-N. He, Ed. *Carbon Dioxide Chemistry*; Science Press: Beijing, 2013. (c) L. Ackermann, *Angew. Chem., Int. Ed.*, 2011, **50**, 3842-3844; (d) K. Huang, C.-L. Sun and Z.-J. Shi, *Chem. Soc. Rev.*, 2011, **40**, 2435-2452; (e) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510-8537; (f) R. Martín and A. W. Kleij, *ChemSusChem*, 2011, **4**, 1259-1263; (g) T. Tsuji and T. Fujihara, *Chem. Commun.*, 2012, **48**, 9956-9964; (h) W. Zhang and X.-B. Lu, *Chin. J. Catal.*, 2012, **33**, 745-756; (i) M. He, Y. Sun and B. Han, *Angew. Chem., Int. Ed.*, 2013, **52**, 9620-9633; (j) L. Zhang and Z. Hou, *Chem. Sci.*, 2013, **4**, 3395-3403; (k) C. Maeda, Y. Miyazaki and T. Ema, *Catal. Sci. Technol.*, 2014, **4**, 1482-1497; (l) M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2014, **114**, 1709-1742; (m) Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 5933; (n) X.-F. Wu and F. Zheng, *Top. Curr. Chem.*, 2017, **375**, 4-63; (o) J. Luo and I. Larrosa, *ChemSusChem*, 2017, **10**, 3317-3332; (p) A. Tortajada, F. Juliá-Hernández, M. Börjesson, T. Moragas and R. Martin, *Angew. Chem., Int. Ed.*, 2018, **57**, 15948-15982; (q) Y.-G Chen, X.-T. Xu, K. Zhang, Y.-Q. Li, L.-P. Zhang, P. Fang and T.-S Mei, *Synthesis,* 2018, **50**, 35-48; (r) J. Hou, J.-S. Li and J. Wu, *Asian J. Org. Chem.*, 2018, **7**, 1439-1447; (s) S.-S. Yan, Q. Fu, L.-L. Liao, G.-Q. Sun, J.-H. Ye, L. Gong, Y.-Z. Bo-Xue and D.-G. Yu, *Coord. Chem. Rev.*, 2018, **374**, 439-463; (t) C. S. Yeung, *Angew. Chem., Int. Ed.*, 2019, **58**, 5492-5502; (u) Z. Zhang, L. Gong, X.-Y. Zhou, S.-S. Yan, J. Li and D.-G. Yu, *Acta Chim. Sinica* 2019, **77**, 783-793; (v) M. D. Burkart, N. Hazari, C. L. Tway and E. L. Zeitler, *ACS Catal.*, 2019, **9**, 7937-7956; (w) Z. Zhang, J.-H. Ye, T. Ju, L.-L. Liao, H. Huang, Y.-Y. Gui, W.-J. Zhou and D.-G. Yu, *ACS Catal.,* 2020, **10**, 10871-10885; (x) C.-K. Ran, X.-W. Chen, Y.-Y. Gui, J. Liu, L, Song, K. Ren and D.-G. Yu, *Sci. China Chem.*, 2020, **63**, 1336-1351; (y) X. He, L.-Q. Qiu, W.-J. Wang, K.-H. Chen and L.-N. He, *Green Chem.*, 2020, **20**, 7301-7320; (z) K.-H. Chen, H.-R. Li and L.-N. He, *Chin. J. Org. Chem.*, 2020, **40**, 2195-2207; (aa) X. Guo, Y. Wang, J. Chen, G. Li and J.-B. Xia, *Chin. J. Org. Chem.*, 2020, **40**, 2208-2220; (ab) C. Zhou, M. Li, J. Yu, S. Sun and Cheng, J. *Chin. J. Org. Chem.,* 2020, **40**, 2221-2231; (ac) B. Limburg, À.

Cristòfol, F. D. Monica and A. W. Kleij, *ChemSusChem*, doi.org/10.1002/cssc.202002246; (ad) Z. Fan, Z. Zhang and C. Xi, *ChemSusChem*, doi.org/10.1002/cssc.202001974; (ae) Z. Chen, S. Du, J. Zhang and X.-F. Wu, *Green Chem.,* DOI: 10.1039/d0gc03280h.

2 For reviews, see: (a) Q.-W. Song, Z.-H. Zhou and L.-N. He, *Green Chem*., 2017, **19**, 3707-3728; **(b)** Z. Zhang, J.-H. Ye, D.-S. Wu, Y.-Q. Zhou, and D.-G. Yu, *Chem*. *Asian*. *J*., 2018, **13**, 2292-2306; (c) S. Wang and C. Xi, *Chem*. *Soc*. *Rev*., 2019, **48**, 382-404; For selected examples, see: (d) T. Toda and Y. Kitagawa, *Angew*. *Chem*., *Int*. *Ed*., 1987, **26**, 334-335; (e) E. García-Egido, I. Fernández and L. Muñoz, *Synth*. *Commun*., 2006, **36**, 3029-3042; (f) Y. Takeda, S. Okumura, S. Tone, I. Sasaki and S. Minakata, *Org*. *Lett*., 2012, **14**, 4874-4877; (g) L. Soldi, C. Massera, M. Costa and N. Della. Ca', *Tetrahedron Lett*., 2014, **55**, 1379; (h) W. J. Yoo, T. V. Nguyen and S. Kobayashi, *Angew*. *Chem*., *Int*. *Ed.*, 2014, **53**, 10213-10217; (i) B. A. Vara, T. J. Struble, W. Wang, M. C. Dobish and J. N. Johnston, *J. Am*. *Chem*. *Soc.,* 2015, **137**, 7302-7305; (j) J.-H. Ye, L. Song, W.-J. Zhou, T. Ju, Z.-B. Yin, S.-S. Yan, Z. Zhang, J. Li and D.-G. Yu, *Angew*. *Chem*., *Int*. *Ed*., 2016, **55**, 10022-10026; (k) J. Rintjema, R. Epping, G. Fiorani, E. Martin, E. C. Escudero-Adán and A. W. Kleij, *Angew*. *Chem*., *Int*. *Ed.*, 2016, **55**, 3972-3976; (l) M.-Y. Wang, Y. Cao, X. Liu, N. Wang, L-N. He and S.-H. Li, *Green Chem*., 2017, **19**, 1240-1244; (m) J.-H. Ye, L. Zhu, S.-S. Yan, M. Miao, X.-C. Zhang, W.-J. Zhou, J. Li, Y. Lan and D.-G. Yu, *ACS Catal*., 2017, **7**, 8324-8330; (n) Z.-B. Yin, J.-H. Ye, W.-J. Zhou, Y.-H. Zhang, L. Ding, Y.-Y. Gui, S.-S. Yan, J. Li and D.-G. Yu, *Org*. *Lett*., 2018, **20**, 190-193; (o) L. Sun, J.-H. Ye, W.-J. Zhou, X. Zeng and D.-G. Yu, *Org*. *Lett*., 2018, **20**, 3049-3052; (p) L. Zhu, J.-H. Ye, M. Duan, X. Qi, D.-G. Yu, R. Bai and Y. Lan, *Org*. *Chem*. *Front*., 2018, **5**, 633-639; (q) R. Yousefi, T. J. Struble, J. L. Payne, M. Vishe, N. D. Schley and J. N. Johnston, *J. Am*. *Chem*. *Soc*., 2019, **141**, 618-625. (r) C.-K. Ran, H. He, X.-H, Li, W. Wang, J.-H. Ye, S.-Y. Yan, B.-Q. Wang, C. Feng and D.-G. Yu, *Chin. J. Chem*., 2020, **38**, 69-76.

3 (a) Z. Zhang, T. Ju, J.-H. Ye and D.-G. Yu, *Synlett,* 2017, **28**, 741; (b) L. Song, Y. -X. Jiang, Z. Zhang, Y.-Y. Gui, X.-Y. Zhou and D.-G. Yu, *Chem. Commun*., 2020, **56**, 8355-8367.

4 For selected C-H carbonylations with CO_2: (a) K. Sasano, J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2013, **135**, 10954-10957; (b) W.-Z. Zhang, S. Liu and X.-B. Lu, *Beilstein J. Org. Chem.*, 2015, **11**, 906-912; (c) Z. Zhang, L.-L. Liao, S.-S. Yan, L. Wang, Y.-Q. He, J.-H. Ye, J. Li, Y.-G. Zhi and D.-G. Yu, *Angew. Chem.*, *Int. Ed.*, 2016, **55**, 7068-7072; (d) W.-Z. Zhang, M.-W. Yang and X.-B. Lu, *Green Chem.*, 2016, **18**, 4181-4184; (e) S. Wang, P. Shao, G. Du and C. Xi, *J. Org. Chem.* 2016, **81**, 6672-6676; (f) W.-Z. Zhang, M.-W. Yang and X.-B. Lu, *Green Chem.*, 2016, **18**, 4181-4184; (g) Z. Zhang, T. Ju, M. Miao, J.-L. Han, Y.-H. Zhang, X.-Y. Zhu, J.-H. Ye, D.-G. Yu and Y.-G. Zhi, *Org. Lett.*, 2017, **19**, 396-399; (h) L. Song, L. Zhu, Z. Zhang, J.-H. Ye, S.-S. Yan, J. Han, Z.-B. Yin, Y. Lan and D.-G. Yu, *Org. Lett*., 2018, **20**, 3776-3799; (i) L. Fu, S. Li, Z. Cai, Y. Ding, X. Guo, L. Zhou, D. Yuan, Q. Sun and G. Li, *Nat. Catal.*, 2018, **1**, 469-478; (j) R. Huang, S. Li, L. Fu and G. Li, *Asian J. Org. Chem.*, 2018, 7, 1376-1379; (k) Z. Zhang, C.-J. Zhu, M. Miao, J.-L. Han, T. Ju, L. Song, J.-H. Ye, J. Li and D.-G. Yu, *Chin. J. Chem.*, 2018, **36**, 430-436; (l) Z. Cai, S. Li, Y. Gao and G. Li, *Adv. Synth. Catal*., 2018, **360**, 4005-4011; (m) W. Li, C. Li and Y. Lyu, *Org. Chem. Front.*, 2018, **5**, 2189-2201; (n) L. Song, G.-M. Cao, W.-J. Zhou, J.-H. Ye, Z. Zhang, X.-Y. Tian, J. Li and D.-G. Yu, *Org. Chem. Front.*, 2018, **5**, 2086-2090; (o) Y. Gao, Z. Cai, S. Li and G. Li, *Org. Lett.*, 2019, **21**, 3663-3699; (p) Z. Zhang, X.-Y. Zhou, J.-G. Wu, L. Song and D.-G. Yu, *Green Chem.*, 2020, **22**, 28-32.

5 (a) T. Onkol, D. S. Dogruer, S. Ito and M. F. Sahin, *Arch. Pharm. Med. Chem.* 2000, **333**, 337-340; (b) R. V. Bonnert, R. C. Brown, D. Chapman, D. R. Cheshire, J. Dixon, F. Ince, E. C. Kinchin, A. J. Lyons, A. M. Davis and C. Hallam, *J. Med. Chem.* 1998, **41**, 4915–4917; (c) M. J. Stocks, L. Alcaraz, A. Bailey, R. Bonnert, E. Cadogan, J. Christie, S. Connolly, A. Cook, A. Fisher, A. Flaherty, S. Hill, A. HumFull Paper phries, A. Ingall, S. Jordan, M. Lawson, A. Mullen, D. Nicholls, S. Paine, G. Pairaudeau, S. St-Gallay and A. Young, *Bioorg. Med. Chem. Lett.* 2011, **21**, 4027–4031; (d) R. P. Austin, P. Barton, R. V. Bonnert, R. C. Brown, P. A. Cage, D. R. Cheshire, A. M. Davis, I. G. Dougall, F. Ince and G. Pairaudeau, *J. Med. Chem*. 2003, **46**, 3210–3020; (e) S. Inoue and T. Kato, *J. Pestic. Sci.* 1983, **8**, 333–338; (f) S. Inoue, T. Uematsu and T. Kato, *J. Pestic. Sci.* 1984, **9**, 689–695.

6 (a) Y. Wan, M. Alterman, M. Larhed and A. Hallberg, *J. Org. Chem.*, 2002, **67**, 6232-6235; (b) X. Wu, A. K. Mahalingam, Y. Wan and M. Alterman, *Tetrahedron Lett.*, 2004, **45**, 4635-4638; (c) L. Troisi, C. Granito, S. Perrone and F. Rosato, *Tetrahedron Lett.*, 2011, **52**, 4330-4332; (d) S. Ding and N. Jiao, *Angew. Chem.*, *Int. Ed.*, 2012, **51**, 9226-9237; (e) B. Yu, H. Zhang, Y. Zhao, S. Chen, J. Xu, L. Hao and Z. Liu, *ACS Catal.*, 2013, **3**, 2076-2089; (f) Y. Jing, R. Liu, Y. Lin and X. Zhou, *Sci. China Chem.*, 2014, **57**, 1117-1125; (g) B. Zhou, H. Hong, H. Wang, T. Zhang, L. Han and N. Zhu, *Eur. J. Org. Chem.*, 2018, **48**, 6983-6900.

7 (a) J. Li, Y. Zhang, Y. Jiang and D. Ma, *Tetrahedron Lett.*, 2012, **53**, 2511-2513; (b) K. E. Ryu, B. R. Kim, G. H. Sueng, H. J. Yoon and Y.-J. Yoon, *Synlett*, 2015, **26**, 1985-1990; (c) H.-X. Weng, Z.-Q. Ji, Y. Chu, C. Cheng and J.-J. Zhang, *Environ Earth Sci.*, 2012, **65**, 561-569; (d) T. Itoh and T. Mase, *Org. Lett.*, 2007, **9**, 3687-3689

8 For recent reviews, see: (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) T. B. Nguyen, *Asian J. Org. Chem.* 2017, **6**, 477.

9 For selected examples, see: (a) L.-L. Sun, C.-L. Deng, R.-Y. Tang and X.-G. Zhang, *J. Org. Chem.*, 2011, **76**, 7546-7550; (b) T. B. Nguyen, L. Ermolenko, P. Retailleau and A. Al-Mourabit, *Angew. Chem.*, *Int. Ed.*, 2014, **53**, 13808-13812; (c) Y. Yang, X. Zhang, W. Zeng, H. Huang and Y. Liang, *RSC Adv.*, 2014, **4**, 6090-6093; (d) Y. Liao, Y. Peng, H. Qi, G.-J. Deng, H. Gong and C.-J. Li, *Chem. Commun.*, 2015, **51**, 1031-1034. (e) F. Chen, G. Liao, X. Li, J. Wu and B.-F. Shi, *Org. Lett.*, 2014, **16**, 5644-5647; (f) L. Meng, T. Fujikawa, M. Kuwayama, Y. Segawa and K. Itami, *J. Am. Chem. Soc.*, 2016, **138**, 10351-10355; (g) H. Xie, J. Cai, Z. Wang, H. Huang and G.-J Deng, *Org. Lett.*, 2016, **18**, 2196-2199; (h) X. Zhu, Y. Yang, G. Xiao, J. Song, Y. Liang and G. Deng, *Chem. Commun.*, 2017, **53**, 11917-11920; (i) M. Wu, Y. Jiang, Z. An, Z. Qi and R. Yan, *Adv. Synth. Catal.*, 2018, **360**, 4236-4240; (j) S. S. E. Ghodsinia and B. Akhlaghinia, *Green Chem.*, 2019, **21**, 3029-3049; (k) A. Dey and A. Hajra, *Org. Lett.*, 2019, **21**, 1686-1689; (l) M. Saito, S. Murakami, T. Nanjo, Y. Kobayashi and Y. Takemoto, *J. Am. Chem. Soc.*, 2020, **142**, 8130-8135; (m) X. Ma, X. Yu, H. Huang, Y. Zhou and Q. Song, *Org. Lett.*, 2020, **22**, 5284-5288; (n) Y. Yue, H. Shao, Z. Wang, K. Wang, L. Wang, K. Zhuo and J. Liu, *J. Org. Chem.*, 2020, **85**, 11265 -11279.

10 (a) H, Xu, H. Deng, Z. Li, H. Xiang and X. Zhou, *Eur. J. Org. Chem.*, 2013, **2013**, 7054-7057; (b) X. Che, J. Jiang, F. Xiao, H. Huang and G.-J. Deng, *Org. Lett.*, 2017, **19**, 4576-4579.