RSC Advances

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *RSC Adv.*, 2022, **12**, 15190

# A facile metal-free one-flask synthesis of multi-substituted furans *via* a $BF_3 \cdot Et_2O$ mediated formal [4 + 1] reaction of 3-chloro-3-phenyldiazirines and α,β-alkenyl ketones†

Zixin Zhang,[a] Aimin Huang,[a] Lin Ma,[a] Jian-hua Xu[b] and Min Zhang *[a]

Received 6th March 2022
Accepted 11th May 2022

DOI: 10.1039/d2ra01472f

rsc.li/rsc-advances

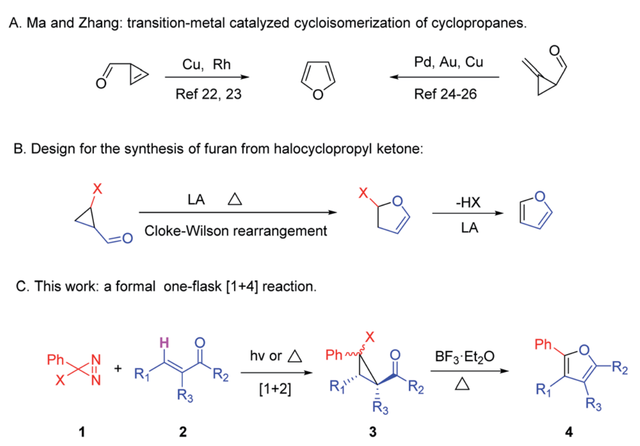
A facile, efficient and metal free one-flask approach to diversely substituted furans from easily accessible 3-chloro-3-phenyldiazirines and α,β-alkenyl ketones is reported. This protocol integrates three steps of cyclopropanation, Cloke–Wilson rearrangement and elimination of HCl in one-flask to give products in moderate to good yields. It provides a metal and oxidant free approach to multi-substituted furans with the advantages of easy operation, mild reaction conditions and a broad scope of substrates.

## Introduction

Furan is a five-membered oxygenated heteroaromatic which is widely spread in natural products[1] and plays an important role in both pharmaceutical chemistry[2,3] and in synthetic organic chemistry as a useful building block.[2,4–6] Long attracting the interests of chemists, a number of synthetic methods for furan have been developed,[3,7–12] including the cyclodehydration of dicarbonyl compounds through Paal–Knorr synthesis[13] and Feist–Bénary cyclocondensation.[14,15] Nevertheless, more selective approaches to multi-substituted furans under mild conditions still remain a challenging task.

In the past decades, cyclopropane has been widely used as a three-carbon synthon to access variable chemicals due to the readiness of ring-opening from high angle and torsion strain and tunable reactivity by substituent-controlled C–C bond polarization/cleavage.[16–21] Transition-metal catalyzed intramolecular ring-opening cycloisomerization of cyclopropenyl ketones[22,23] or alkylidene cyclopropyl ketones[24–26] has been proved to be a very successful and reliable approach to furans (Scheme 1A). Early in 2003, Ma and Zhang[22] developed a regioselective cycloisomerization of cyclopropenyl ketones using copper(I) or Pd catalysts. Later in 2004, they developed a Pd mediated ring-opening cycloisomerization of 2-methylene- or alkylidene cyclopropyl ketone to di- or tri-substituted furans.[24] In 2007, Liang group reported a synthesis of trisubstituted furans *via* a Cu(I)-catalyzed formal [4 + 1] cycloaddition of α,β-alkynyl ketones with diazoacetates.[27] Xu and co-workers further developed a Cu–Pd relay catalysis to access tetra-substituted furans from cyclopropenes.[28] These elegant transition-metal catalyzed methods are advantageous in both atom economy and efficiency. However, using alternative non-metal catalysts to promote cycloisomerization is very essential in account of economic, environmental and sustainability requirement. Recently, Wang and coworkers[29–31] have developed $I_2/K_2CO_3$ or DBU mediated ring opening and cyclization of cyano-substituted cyclopropyl ketones to afford furan derivatives.

The Cloke–Wilson rearrangement (CWR) reaction has been intensively used to access dihydrofurans from cyclopropyl ketones.[32–37] Besides transition-metal catalysis,[38,39] CWR reaction can also be promoted by Lewis acid,[40,41] photocatalysis,[42–44] and organo-catalysis.[26,32,33] Regrettably, an extra dehydrogenation procedure is a prerequisite to transform dihydrofurans to furans using stoichiometric oxidants such as DDQ.[45,46] To avoid




Scheme 1 Synthesis of furan from cyclopropanes by literature and this work.

[a]School of Chemistry and Chemical Engineering, Guangxi University, Nanning, Guangxi 530004, China. E-mail: chemizhang@gxu.edu.cn
[b]School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, China

† Electronic supplementary information (ESI) available. See https://doi.org/10.1039/d2ra01472f

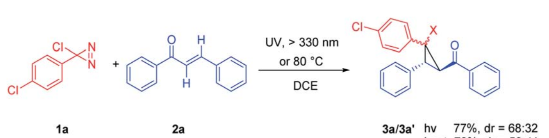
the harmful oxidation procedure, we envisioned that halocyclopropyl ketone is an ideal alternative precursor to perform CWR reaction to deliver halogenated dihydrofuran, which is converted to furan *via* elimination of HX (Scheme 1B). However, there are few reports making use of this elimination strategy. As an elegant example, Namboothiri's group reported that acidic $Al_2O_3$ could be used to promote CWR reaction of dibromocyclopropyl ketone followed by elimination to access 3-bromo furans.[47,48]

Taking advantage of the fact that the highly reactive halocarbenes (RCX) derived from the easily available 3-halodiazirines ($RCN_2X$) upon the loss of $N_2$ readily take part in [2 + 1] cycloaddition with alkenes to give halogenated cyclopropanes,[49–52] we design a formal [4 + 1] approach to furans using this cyclopropanation method to obtain the required halocyclopropyl ketone precursors (Scheme 1C). Firstly, photolysis or thermolysis of 3-halo-3-phenyldiazirine **1** in the presence of α,β-alkenyl ketone **2** gives the halocyclopropyl ketone **3**, which is then subjected to a tandem CWR–elimination reaction sequence to afford the furan **4**. We further succeeded in using the same Lewis acid to promote both the CWR and the elimination reactions to facilitate the reaction procedure. As a result, we herein report a one-flask metal-free synthetic approach to a diversity of di-, tri- or tetra-substituted furans from a series of 3-halo-3-phenyldiazirines and α,β-alkenyl ketones *via* cyclopropanation and $BF_3\cdot Et_2O$ mediated CWR–elimination reactions.

## Results and discussions

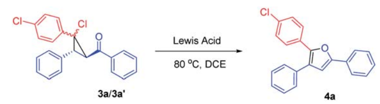
Initially, the synthesis of halocyclopropyl ketones was investigated (Scheme 2). Photolysis or thermolysis of 3-chloro-3-(4-chlorophenyl)diazirine (**1a**) was used to generate phenylchlorocarbene (PhCCl) *in situ*, which rapidly reacted with chalcone (**2a**) to give the halocyclopropyl ketone diastereomers (**3a**/**3a′**). After an optimization of solvents and temperatures (for details, please see Table S1†), either photolysis at room temperature or thermolysis at 80 °C in 1,2-dichloroethane (DCE) gave the halocyclopropyl ketones (**3a**/**3a′**) in highest yield with similar diastereoselectivity.

Next, the transformation of halocyclopropyl ketone **3a** (major isomer) to furan **4a** was investigated and selected results are summarized in Table 1 (for more details, see Table S2†). Lewis acid promoters $FeCl_3\cdot 6H_2O$, $TiCl_4$ and $FeCl_2\cdot 4H_2O$ were the most efficient catalysts for this conversion (0.08–0.5 h), while $BF_3\cdot Et_2O$, $AlCl_3$, $SnCl_4$ and $Sc(OTf)_3$ promoted the reaction less efficiently (15–45 h). Delightfully, furan **4a** was obtained in excellent yields (85–98%) in the presence of these seven catalysts (entries 1–7). On the contrary, $BiCl_3$ couldn't complete this transformation in 72 h and gave **4a** in lower yield




Scheme 2 Synthesis of halo-cyclopropyl ketone **3a**/**3a′**.

Table 1 Screening of Lewis acids for **4a**[a]




| Entry | Lewis acid | Time, h | Yield,[b] % |
|---|---|---|---|
| 1 | $TiCl_4$ | 0.16 | 86 |
| 2 | $FeCl_2\cdot 4H_2O$ | 0.5 | 96 |
| 3 | $FeCl_3\cdot 6H_2O$ | 0.08 | 86 |
| 4 | $BF_3\cdot Et_2O$ | 15 | 98 |
| 5 | $AlCl_3$ | 17 | 90 |
| 6 | $SnCl_4$ | 21 | 87 |
| 7 | $Sc(OTf)_3$ | 45 | 86 |
| 8 | $BiCl_3$ | 72 | 68[c] |
| 9 | None | 24 | NR |
| 10 | PTSA | 36 | 90 |
| 11[d] | $FeCl_2\cdot 4H_2O$ | 1 | 97 |
| 12[e] | $BF_3\cdot Et_2O$ | 16 | 98 |
| 13[d,e] | $FeCl_2\cdot 4H_2O$ | 1 | 97 |

[a] Reagents and conditions: halocyclopropyl ketone **3a** (0.06 mmol), Lewis acid (0.06 mmol, 1 eq.) in 5 mL DCE was heated at 80 °C in a 38 mL reaction tube equipped with a condenser until the reaction was completed by TLC monitoring. NR = no reaction. RSM = recovery of starting material. [b] Isolated yield. [c] Yield is based on consumed halocyclopropyl ketone. RSM was 16%. [d] 0.2 eq. LA was used. [e] **3a′** was used instead of **3a**.

(entry 8). No reaction could take place in the absence of a Lewis acid (entry 9). Brønsted acid *para*-toluene sulfonic acid (PTSA) could also mediate this reaction to give **4a** in 90% yield in 36 h (entry 10). Therefore, among these promoters, $BF_3\cdot Et_2O$ and $FeCl_2\cdot 4H_2O$ showed the best catalytic activity to give nearly quantitative yields of **4a**. It is also noted that the halocyclopropyl ketone diastereomer **3a′** was similarly converted to **4a** in the nearly quantitative yield as **3a** in the presence of either $BF_3\cdot Et_2O$ or $FeCl_2\cdot 4H_2O$ (entries 12–13). Therefore, there is no need to separate two diastereomers **3a**/**3a′** for the transformation to **4a**. We then succeeded in implementing these reaction steps in one-flask (for details, please see Table S3†) with $BF_3\cdot Et_2O$ (1 eq.) as the best catalyst, which was added into the flask after the completion of cyclopropanation to avoid side reactions. This one-flask protocol gave **4a** in an overall yield of 68%.

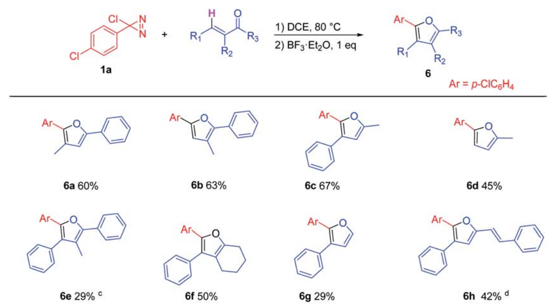
With this optimized one-flask conditions in hand, we investigated the scope of *para*-substituted phenylchlorodiazirines **1** (Table 2). Unsubstituted (R = H) or substituted phenylchlorodiazirines with either electron-donating (R = Me, OMe) or slightly electron withdrawing (R = F, Cl) groups on the phenyl ring gave furans (**4a–4e**) in good yields (57–71%). However, the cyclopropyl ketones with strong electron-withdrawing substituents such as $CF_3$ or CN (**3f**, **3g**) need to be heated in *n*-octane at 120 °C to give furans in reasonable yields (**4f** 43%; **4g** 42%) due to lower ring opening reactivity for less polarization character of C–C bond. This conversion could also be driven by the powerful $FeCl_3\cdot 6H_2O$ and gave furans in better yields (**4f** 57%; **4g** 53%). However, the reaction of 3-benzyl-3-chloro-diazirine ($PhCH_2CClN_2$) and chalcone couldn't afford the expected furan. The scope of chalcones were also investigated: chalcones with substituents on either phenyl ring gave furans (**5a–5i; 5m–5t**) in good yields (70–80%), no matter they are electron-withdrawing or electron-donating. This one-flask strategy can also be applied to the naphthyl, thiophenyl or pyridinyl substituted chalcones to afford furans (**5j–5l, 5u**) with moderate to good yields (40–78%).

We further extended this one-flask reaction to a wide range of alkenyl ketones with alkyl groups, and the corresponding furans were obtained in moderate to good yields (Table 3). Alkenyl ketones substituted with a methyl group at $R_1$, $R_2$ or $R_3$ position gave trisubstituted furans **6a–6c** in good yields (60–67%). Methyl vinyl ketone (MVK) gave 2-methyl-5-phenyl furan **6d** in 45% yield. Notably, this protocol enabled an astonishing access to tetra-substituted furans with structural complexity (**6e**, **6f**). For example, 2-benzylidenecyclohexan-1-one gave tetra-substituted furan **6f** with a fused ring in good yield (50%). This protocol can also be applied to α,β-unsaturated aldehydes, *e.g.*, cinnamaldehyde was used to synthesize 2,3-disubstituted furan **6g** in 29% yield. Bis(2-phenylvinyl) ketone gave furan **6h** in 42% yield, exemplifying the functional group tolerance for another sensitive C═C double bond. Step-by-step analysis of these two-stage reactions (Table S5†) reveals that the lower yields were owing to the poor cyclopropanation reactivity because of less electronic richness (**6d**, **6g**) or steric hindrance (**6e**) of the C═C double bond, in which a considerable amount of carbene dimer was often generated as side product. Therefore, this one-flask protocol can use a variety of α,β-unsaturated carbonyl substrates to synthesize 2,3- or 2,5-disubstituted, 2,3,5-trisubstituted and even 2,3,4,5-tetrasubstituted furans with moderate to good yields.

To probe the mechanism of these reactions, β-methyl chalcone was subjected to this one-flask reaction (Scheme 3A). Unlike the α-methyl chalcone, the CWR–elimination reaction of the cyclopropyl ketone promoted by $BF_3$ gave a complicated mixture without any furan product, indicating the necessity of a β-hydrogen. Reactivities of other 3-halo-3-phenyldiazirines (X = Br, F) were also studied (Scheme 3B). 3-Bromo-3-phenyldiazirine (**1ab**) gave bromocyclopropyl ketone **3ab**/**3ab′** in 2 h (72%), which gave furan **4a** in 95% yield in 17 h with the similar reactivity as **3a**/**3a′** (X = Cl). It indicates that $BF_3$ is supposed to bind with the oxygen in carbonyl group instead of halogen to promote the CWR reaction, leading to no significant difference in the reactivities between **3a** and **3ab** (Scheme 4, path a). On the other hand, 3-fluoro-3-phenyldiazirine (**1ac**) gave the cyclopropyl ketone **3ac** (59%) much slower (48 h) owing to the less electrophilicity and stability of phenylfluorocarbene (PhCF).[53,54] Moreover, **3ac** is quite ready to give furan **4a** in 90% yield with excellent reactivity (2 h). This efficient transformation is supposed to be attributed to a different pathway because of the high affinity between $BF_3$ and fluorine (*vide infra*).

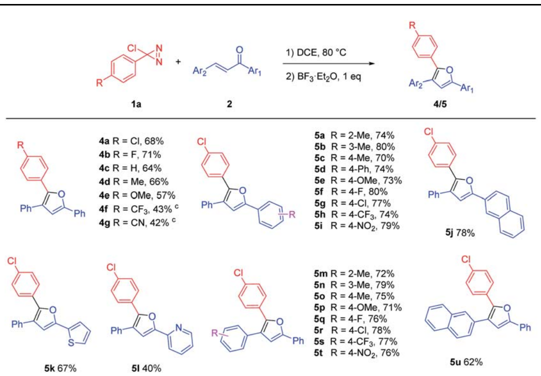
Based on these experiments and literature,[34,47,55] a plausible mechanism is proposed in Scheme 4. Upon thermolysis or photolysis, 3-halo-3-phenyldiazirine (**1**) generates electrophilic singlet phenylhalocarbene (PhCX) with the loss of nitrogen

Table 3 Scope of alkyl substituted alkenyl ketones[a,b]

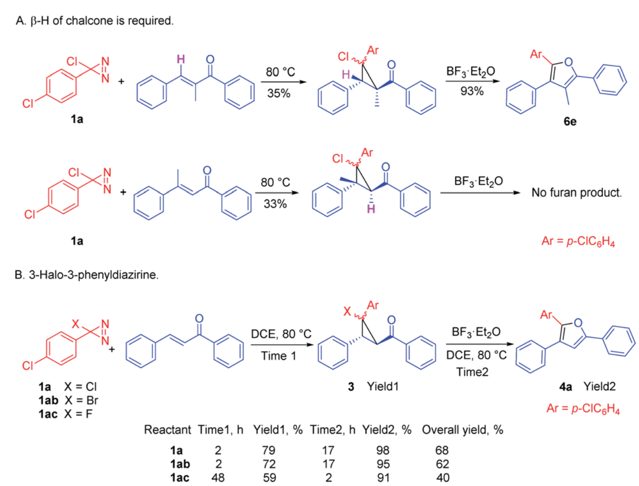



[a] Reagents and conditions: using method A as above unless specified. [b] Isolated yield of one-flask reaction. [c] **1a** (0.2 mmol) was reacted with 2 eq. alkenyl ketone (0.4 mmol). [d] Two equivalents of alkenyl ketone were used and reactions were performed at 60 °C in both stages.

Table 2 Scope of substrates[a,b]

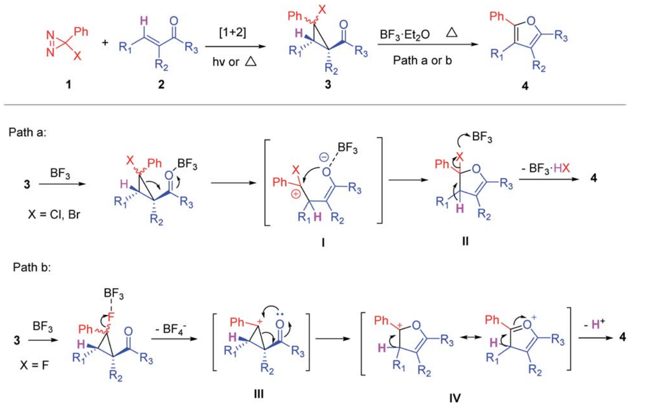



[a] Reagents and conditions (method A): 3-aryl-3-chlorodiazirine **1** (0.2 mmol), alkenyl ketone **2** (0.2 mmol) in 5 mL DCE was heated at 80 °C in a 38 mL reaction tube with a condenser until the reaction was completed (usually 2 h). $BF_3 \cdot Et_2O$ (0.2 mmol, 1 eq.) was added in and kept on heating to complete the transformation. [b] Isolated yield of one-flask reaction. [c] Reacted at 120 °C in *n*-octane and $BF_3 \cdot Et_2O$ (5 eq.) was used.




Scheme 3 Control experiments.



Scheme 4 Plausible mechanism.

($N_2$).[51,56] The PhCX carbene reacts rapidly with α,β-alkenyl ketone (**2**) to afford halocyclopropyl ketone (**3**) *via* a [2 + 1] cycloaddition. Subsequent addition of $BF_3 \cdot Et_2O$ catalyzes the CWR rearrangement of chloro- or bromocyclopropyl ketone **3a**/**3ab** by complexing with the carbonyl oxygen in **3** (path a) to facilitate the heterolytic cleavage of this donor–acceptor cyclopropane to give the key zwitterion intermediate **I**. Then, an intramolecular cyclization of **I** by nucleophilic attack of oxyanion to carbocation gives dihydrofuran **II**, which is converted to furan **4** after the loss of HX with the aid of $BF_3$. In the case of fluorocyclopropyl ketone **3ac**, the ring-opening might be driven by the loss of tetrafluoroborate ($BF_4^-$) and proceeds through a cyclopropyl carbocation mechanism in a similar intramolecular cyclization mode (path b).

# Conclusions

In conclusion, we have developed a facile one-flask approach to the di-, tri- and even tetra-substituted furans in moderate to good yields from readily available starting materials using inexpensive boron trifluoride as catalyst. This metal and oxidant free method involves the cyclopropanation of α,β-alkenyl ketones with phenylchlorocarbene, $BF_3$ mediated ring-opening cycloisomerization (Cloke–Wilson rearrangement) and elimination of HCl to give the multi-substituted furans. This method has the advantages of simple operation, mild reaction conditions and a broad scope of substrates, which provides a concise approach to diversified biologically and synthetically useful furans. We believe it will benefit the discovery of new application of furan derivatives.

# Author contributions

Z. Zhang: most of the experimental work and writing of ESI.† A. Huang & L. Ma: methodology and discussion. J. Xu: manuscript revision and discussion. M. Zhang: conceptualization, funding acquisition, supervision, and writing, review, and editing of the manuscript.

# Conflicts of interest

The authors declare no competing financial interest.

# Acknowledgements

We thank the National Natural Science Foundation of China (No. 21861002, 21462003) for financial support.

# Notes and references

1 Z. Batool, D. Xu, X. Zhang, X. Li, Y. Li, Z. Chen, B. Li and L. Li, A review on furan: formation, analysis, occurrence, carcinogenicity, genotoxicity and reduction methods, *Crit. Rev. Food Sci.*, 2021, **61**, 395–406.
2 H.-K. Lee, K.-F. Chan, C.-W. Hui, H.-K. Yim, X.-W. Wu and H. N. C. Wong, Use of furans in synthesis of bioactive compounds, *Pure Appl. Chem.*, 2005, **77**, 139–143.
3 A. Blanc, V. Bénéteau, J.-M. Weibel and P. Pale, Silver & gold-catalyzed routes to furans and benzofurans, *Org. Biomol. Chem.*, 2016, **14**, 9184–9205.
4 B. H. Lipshutz, Five-membered heteroaromatic rings as intermediates in organic synthesis, *Chem. Rev.*, 1986, **86**, 795–819.
5 H. N. C. Wong, P. Yu and C. Y. Yick, The use of furans in natural product syntheses, *Pure Appl. Chem.*, 1999, **71**, 1041–1044.
6 A. S. Makarov, M. G. Uchuskin and I. V. Trushkov, Furan Oxidation Reactions in the Total Synthesis of Natural Products, *Synthesis*, 2018, **50**, 3059–3086.
7 X. L. Hou, H. Y. Cheung, T. Y. Hon, P. L. Kwan, T. H. Lo, S. Y. Tong and H. N. C. Wong, Regioselective syntheses of substituted furans, *Tetrahedron*, 1998, **54**, 1955–2020.
8 R. C. D. Brown, Developments in Furan Syntheses, *Angew. Chem., Int. Ed.*, 2005, **44**, 850–852.
9 S. F. Kirsch, Syntheses of polysubstituted furans: recent developments, *Org. Biomol. Chem.*, 2006, **4**, 2076–2080.
10 N. T. Patil and Y. Yamamoto, Coinage Metal-Assisted Synthesis of Heterocycles, *Chem. Rev.*, 2008, **108**, 3395–3442.
11 A. Deepthi, B. P. Babu and A. L. Balachandran, Synthesis of Furans - Recent Advances, *Org. Prep. Proced. Int.*, 2019, **51**, 409–442.
12 D. X. Duc, Recent Progress in the Synthesis of Furan, *Mini-Rev. Org. Chem.*, 2019, **16**, 422–452.
13 G. Minetto, L. F. Raveglia, A. Sega and M. Taddei, Microwave-Assisted Paal–Knorr Reaction – Three-Step Regiocontrolled Synthesis of Polysubstituted Furans, Pyrroles and Thiophenes, *Eur. J. Org. Chem.*, 2005, 5277–5288.
14 M. A. Calter, C. Zhu and R. J. Lachicotte, Rapid Synthesis of the 7-Deoxy Zaragozic Acid Core, *Org. Lett.*, 2002, **4**, 209–212.
15 G. Mross, E. Holtz and P. Langer, Synthesis of 2-Alkenyl-3-(alkoxycarbonyl)furans Based on Feist–Benary Cyclocondensation of (2,4-Dioxobutylidene)phosphoranes with α-Haloketones and α-Chloracetaldehyde, *J. Org. Chem.*, 2006, **71**, 8045–8049.

16 H.-U. Reissig and R. Zimmer, Donor–Acceptor-Substituted Cyclopropane Derivatives and Their Application in Organic Synthesis, *Chem. Rev.*, 2003, **103**, 1151–1196.
17 M. A. Cavitt, L. H. Phun and S. France, Intramolecular donor–acceptor cyclopropane ring-opening cyclizations, *Chem. Soc. Rev.*, 2014, **43**, 804–818.
18 T. F. Schneider, J. Kaschel and D. B. Werz, A New Golden Age for Donor–Acceptor Cyclopropanes, *Angew. Chem., Int. Ed.*, 2014, **53**, 5504–5523.
19 K. R. Babu, X. He and S. Xu, Lewis Base Catalysis Based on Homoconjugate Addition: Rearrangement of Electron-Deficient Cyclopropanes and Their Derivatives, *Synlett*, 2020, **31**, 117–124.
20 Y. Xia, X. Liu and X. Feng, Asymmetric Catalytic Reactions of Donor–Acceptor Cyclopropanes, *Angew. Chem., Int. Ed.*, 2021, **60**, 9192–9204.
21 T. R. McDonald, L. R. Mills, M. S. West and S. A. L. Rousseaux, Selective Carbon–Carbon Bond Cleavage of Cyclopropanols, *Chem. Rev.*, 2021, **121**, 3–79.
22 S. Ma and J. Zhang, 2,3,4- or 2,3,5-Trisubstituted furans: catalyst-controlled highly regioselective ring-opening cycloisomerization reaction of cyclopropenyl ketones, *J. Am. Chem. Soc.*, 2003, **125**, 12386–12387.
23 A. Padwa, J. M. Kassir and S. L. Xu, Rhodium-catalyzed ring-opening reaction of cyclopropenes. Control of regioselectivity by the oxidation state of the metal, *J. Org. Chem.*, 2002, **56**, 6971–6972.
24 S. Ma and J. Zhang, Tuning the Regioselectivity in the Palladium(II)-Catalyzed Isomerization of Alkylidene Cyclopropyl Ketones: A Dramatic Salt Effect, *Angew. Chem., Int. Ed.*, 2003, **42**, 183–187.
25 S. Ma, L. Lu and J. Zhang, Catalytic Regioselectivity Control in Ring-Opening Cycloisomerization of Methylene- or Alkylidenecyclopropyl Ketones, *J. Am. Chem. Soc.*, 2004, **126**, 9645–9660.
26 X. He, Y. Tang, Y. Wang, J. B. Chen, S. Xu, J. Dou and Y. Li, Phosphine-Catalyzed Activation of Alkylidenecyclopropanes: Rearrangement to Form Polysubstituted Furans and Dienones, *Angew. Chem., Int. Ed.*, 2019, **58**, 10698–10702.
27 L.-B. Zhao, Z.-H. Guan, Y. Han, Y.-X. Xie, S. He and Y.-M. Liang, Copper-Catalyzed [4 + 1] Cycloadditions of α,β-Acetylenic Ketones with Diazoacetates to Form Trisubstituted Furans, *J. Org. Chem.*, 2007, **72**, 10276–10278.
28 C. Song, J. Wang and Z. Xu, Tandem metal relay catalysis: from cyclopropene to polysubstituted furan, *Org. Biomol. Chem.*, 2014, **12**, 5802–5806.
29 W. Ye, C. Tan, J. Yao, S. Xue, Y. Li and C. Wang, Iodine-Promoted Domino Reactions of 1-Cyanocyclopropane 1-Esters: A Straightforward Approach to Fully Substituted 2-Aminofurans, *Adv. Synth. Catal.*, 2016, **358**, 426–434.
30 J.-M. Liu, X.-Y. Liu, X.-S. Qing, T. Wang and C.-D. Wang, $I_2$/$K_2CO_3$-Promoted ring-opening/cyclization/rearrangement/aromatization sequence: a powerful strategy for the synthesis of polysubstituted furans, *Chin. Chem. Lett.*, 2017, **28**, 458–462.
31 Z. Su, Z. Xie, S. Wang, N. Luo and C. Wang, Direct synthesis of highly functionalized furans from donor-acceptor cyclopropanes via DBU-mediated ring expansion reactions, *Org. Biomol. Chem.*, 2019, **17**, 7342–7351.
32 J. Zhang, Y. Tang, W. Wei, Y. Wu, Y. Li, J. Zhang, Y. Zheng and S. Xu, Organocatalytic Cloke-Wilson Rearrangement: DABCO-Catalyzed Ring Expansion of Cyclopropyl Ketones to 2,3-Dihydrofurans, *Org. Lett.*, 2017, **19**, 3043–3046.
33 W. Wei, Y. Tang, Y. Zhou, G. Deng, Z. Liu, J. Wu, Y. Li, J. Zhang and S. Xu, Recycling Catalyst as Reactant: A Sustainable Strategy to Improve Atom Efficiency of Organocatalytic Tandem Reactions, *Org. Lett.*, 2018, **20**, 6559–6563.
34 Q. Shi, Y. Wang and D. Wei, Theoretical study on DABCO-catalyzed ring expansion of cyclopropyl ketone: mechanism, chemoselectivity, and role of catalyst, *Comput. Theor. Chem.*, 2018, **1123**, 20–25.
35 A. Ortega, R. Manzano, U. Uria, L. Carrillo, E. Reyes, T. Tejero, P. Merino and J. L. Vicario, Catalytic Enantioselective Cloke–Wilson Rearrangement, *Angew. Chem., Int. Ed.*, 2018, **57**, 8225–8229.
36 H. Nambu, Y. Onuki, N. Ono and T. Yakura, Iodide-Catalyzed Ring-Opening Cyclization of Cyclohexane-1,3-dione-2-spirocyclopropanes, *Adv. Synth. Catal.*, 2018, **360**, 2938–2944.
37 X. Liang, P. Guo, W. Yang, M. Li, C. Jiang, W. Sun, T. P. Loh and Y. Jiang, Stereoselective synthesis of trifluoromethyl-substituted 2H-furan-amines from enaminones, *Chem. Commun.*, 2020, **56**, 2043–2046.
38 R. K. Bowman and J. S. Johnson, Nickel-catalyzed rearrangement of 1-acyl-2-vinylcyclopropanes. A mild synthesis of substituted dihydrofurans, *Org. Lett.*, 2006, **8**, 573–576.
39 M. L. Piotrowski and M. A. Kerr, Tandem Cyclopropanation/Vinylogous Cloke–Wilson Rearrangement for the Synthesis of Heterocyclic Scaffolds, *Org. Lett.*, 2018, **20**, 7624–7627.
40 V. K. Yadav and R. Balamurugan, Silicon-assisted ring opening of donor-acceptor substituted cyclopropanes. An expedient entry to substituted dihydrofurans, *Org. Lett.*, 2001, **3**, 2717–2719.
41 Y. Y. Zhu, M. L. Zhang, T. Li and X. X. Song, $AlCl_3$-Promoted Stereospecific Cloke-Wilson Rearrangement of Spirocyclopropyl Barbiturates for the Synthesis of Substituted Dihydrofuro[2,3-d]pyrimidines, *ChemistrySelect*, 2019, **4**, 10838–10842.
42 D. Kalpogiannaki, C.-I. Martini, A. Nikopoulou, J. A. Nyxas, V. Pantazi and L. P. Hadjiarapoglou, Fused dihydrofurans from the one-pot, three-component reaction of 1,3-cyclohexanedione, iodobenzene diacetate and alkenes, *Tetrahedron*, 2013, **69**, 1566–1575.
43 C.-H. Lin, D. Pursley, J. E. M. N. Klein, J. Teske, J. A. Allen, F. Rami, A. Köhn and B. Plietker, Non-decarbonylative photochemical versus thermal activation of $Bu_4N[Fe(CO)_3(NO)]$ – the Fe-catalyzed Cloke–Wilson rearrangement of vinyl and arylcyclopropanes, *Chem. Sci.*, 2015, **6**, 7034–7043.
44 J. Luis-Barrera, V. Laina-Martín, T. Rigotti, F. Peccati, X. Solans-Monfort, M. Sodupe, R. Mas-Ballesté, M. Liras and J. Alemán, Visible-Light Photocatalytic Intramolecular

Cyclopropane Ring Expansion, *Angew. Chem., Int. Ed.*, 2017, **56**, 7826–7830.
45 N. M. Barl, E. Sansiaume-Dagousset, G. Monzón, A. J. Wagner and P. Knochel, Preparation and Reactions of Heteroarylmethylzinc Reagents, *Org. Lett.*, 2014, **16**, 2422–2425.
46 A. Lévesque, T. Maris and J. D. Wuest, ROY Reclaims Its Crown: New Ways to Increase Polymorphic Diversity, *J. Am. Chem. Soc.*, 2020, **142**, 11873–11883.
47 N. Satam, S. Nemu, G. N. Gururaja and I. N. N. Namboothiri, Substrate-oriented selectivity in the Mg-mediated conjugate addition of bromoform to electron-deficient alkenes, *Org. Biomol. Chem.*, 2020, **18**, 5697–5707.
48 E. Gopi and I. N. N. Namboothiri, Synthesis of Fused Bromofurans via Mg-Mediated Dibromocyclopropanation of Cycloalkanone-Derived Chalcones and Cloke–Wilson Rearrangement, *J. Org. Chem.*, 2013, **78**, 910–919.
49 R. A. Moss, Diazirines: Carbene Precursors Par Excellence, *Acc. Chem. Res.*, 2006, **39**, 267–272.
50 M. Zhang, R. A. Moss, J. Thompson and K. Krogh-Jespersen, Evolution of Structure and Reactivity in a Series of Iconic Carbenes, *J. Org. Chem.*, 2012, **77**, 843–850.
51 L. Wang, K. Krogh-Jespersen and R. A. Moss, Activation Parameters for Additions to Alkenes of Arylchlorocarbenes with Enhanced Electrophilicity, *J. Org. Chem.*, 2015, **80**, 7590–7593.
52 E. M. D. Allouche and A. B. Charette, Cyclopropanation Reactions of Semi-stabilized and Non-stabilized Diazo Compounds, *Synthesis*, 2019, **51**, 3947–3963.
53 R. A. Moss, Carbenic selectivity in cyclopropanation reactions, *Acc. Chem. Res.*, 1980, **13**, 58–64.
54 I. R. Gould, N. J. Turbo, J. Butcher, C. Doubleday, N. P. Hacker, G. F. Lehr, R. A. Moss, D. P. Cox, W. Guo, R. C. Munjal, L. A. Perez and M. Fedorynski, Time-resolved flash spectroscopic investigations of the reactions of singlet arylhalocarbenes, *Tetrahedron*, 1985, **41**, 1587–1600.
55 T. Li, D. Yan, C. Cui, X. Song and J. Chang, A thermal decarboxylative Cloke-Wilson rearrangement of dispirocyclopropanes derived from para-quinone methides and bromo-Meldrum's acids: an approach to synthesize spirobutyrolactone para-dienones, *Org. Chem. Front.*, 2020, **7**, 2682–2688.
56 G. Richter, E. Mendez-Vega and W. Sander, Singlet Halophenylcarbenes as Strong Hydrogen-Bond Acceptors, *J. Phys. Chem. A*, 2016, **120**, 3524–3532.