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A facile metal-free one-flask synthesis of multi-substituted furans *via* a $\text{BF}_3 \cdot \text{Et}_2\text{O}$ mediated formal [4 + 1] reaction of 3-chloro-3-phenyldiazirines and α, β -alkenyl ketones†

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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

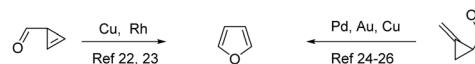
Furan is a five-membered oxygenated heteroaromatic which is widely spread in natural products¹ and plays an important role in both pharmaceutical chemistry^{2,3} and in synthetic organic chemistry as a useful building block.^{2,4–6} Long attracting the interests of chemists, a number of synthetic methods for furan have been developed,^{3,7–12} including the cyclodehydration of dicarbonyl compounds through Paal–Knorr synthesis¹³ 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 Zhang²² developed a regio-selective 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

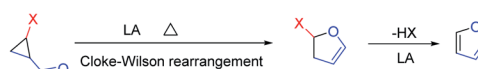
developed a Cu–Pd relay catalysis to access tetra-substituted furans from cyclopropanes.²⁸ These elegant transition-metal catalyzed methods are advantageous in both atom economy and efficiency. However, using alternative non-metal catalysts to promote cycloisomerization is very essential in account of economic, environmental and sustainability requirement. Recently, Wang and coworkers^{29–31} have developed $\text{I}_2/\text{K}_2\text{CO}_3$ 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

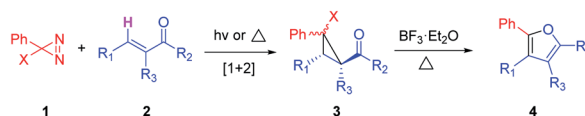
A. Ma and Zhang: transition-metal catalyzed cycloisomerization of cyclopropanes.



B. Design for the synthesis of furan from halocyclopropyl ketone:



C. This work: a formal one-flask [1+4] reaction.



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

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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 Al₂O₃ 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 halocarbene (RCX) derived from the easily available 3-halodiazirines (RCN₂X) upon the loss of N₂ 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 BF₃·Et₂O 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 FeCl₃·6H₂O, TiCl₄ and FeCl₂·4H₂O were the most efficient catalysts for this conversion (0.08–0.5 h), while BF₃·Et₂O, AlCl₃, SnCl₄ 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, BiCl₃ 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 ·4H ₂ O | 0.5 | 96 |
| 3 | FeCl ₃ ·6H ₂ O | 0.08 | 86 |
| 4 | BF ₃ ·Et ₂ O | 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 ·4H ₂ O | 1 | 97 |
| 12 ^e | BF ₃ ·Et ₂ O | 16 | 98 |
| 13 ^{d,e} | FeCl ₂ ·4H ₂ O | 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, BF₃·Et₂O and FeCl₂·4H₂O 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 BF₃·Et₂O or FeCl₂·4H₂O (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 BF₃·Et₂O (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%.

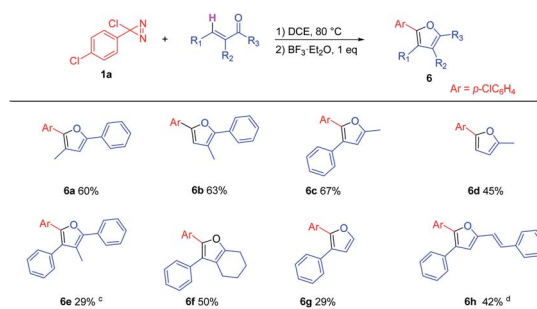
With this optimized one-flask conditions in hand, we investigated the scope of *para*-substituted phenylchlorodiazirines **1** (Table 2). Unsubstituted (R = H) or substituted phenylchlorodiazirines with either electron-donating (R = Me, OMe) or slightly electron withdrawing (R = F, Cl) groups on the phenyl ring gave furans (**4a–4e**) in good yields (57–71%). However, the cyclopropyl ketones with strong electron-withdrawing substituents such as CF₃ 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 FeCl₃·6H₂O and gave furans in better yields (**4f** 57%; **4g** 53%). However, the reaction of 3-benzyl-3-chloro-diazirine (PhCH₂CCLN₂) 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 R₁, R₂ or R₃ 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-benzylidencyclohexan-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 BF₃ gave a complicated

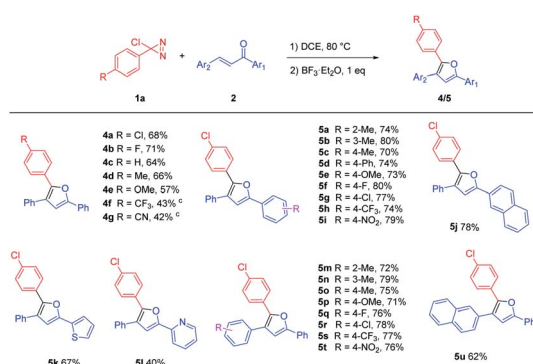
Table 3 Scope of alkyl substituted alkenyl ketones^{a,b}

^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.

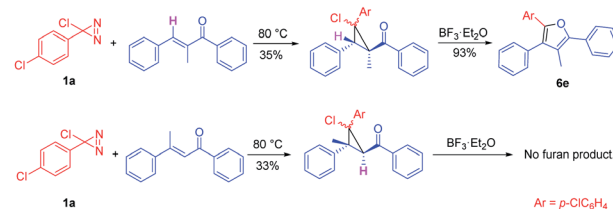
mixture without any furan product, indicating the necessity of a β -hydrogen. Reactivities of other 3-halo-3-phenyldiazirines (X = Br, F) were also studied (Scheme 3B). 3-Bromo-3-phenyldiazirine (**1ab**) gave bromocyclopropyl ketone **3ab/3ab'** in 2 h (72%), which gave furan **4a** in 95% yield in 17 h with the similar reactivity as **3a/3a'** (X = Cl). It indicates that BF₃ 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 BF₃ 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

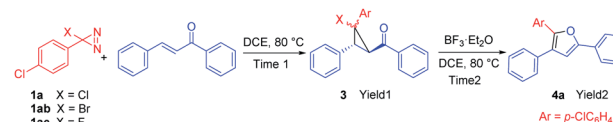
Table 2 Scope of substrates^{a,b}

^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). BF₃·Et₂O (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 BF₃·Et₂O (5 eq.) was used.

A. β -H of chalcone is required.



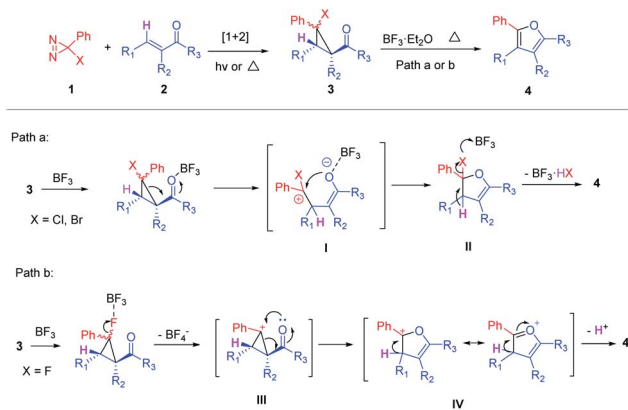
B. 3-Halo-3-phenyldiazirine.



| Reactant | Time1, h | Yield1, % | Time2, h | Yield2, % | Overall yield, % |
|------------|----------|-----------|----------|-----------|------------------|
| 1a | 2 | 79 | 17 | 98 | 68 |
| 1ab | 2 | 72 | 17 | 95 | 62 |
| 1ac | 48 | 59 | 2 | 91 | 40 |

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.

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