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N-Heterocyclic Carbene Catalyzed Synthesis of Trisubstituted Epoxides via Tandem Amidation/Epoxidation Sequence

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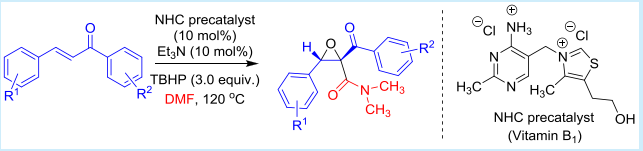
ABSTRACT: A tandem amidation/epoxidation sequence between various substituted chalcones and *N,N*-dimethylformamide (DMF) for the synthesis of trisubstituted epoxides employing N-heterocyclic carbene catalysis was developed. This reaction was performed under metal-free conditions in the presence of *tert*-butyl hydroperoxide (TBHP) as the oxidant. Trisubstituted epoxides bearing a ketone and an amide functionality (*N,N*-dimethyl formyl group) were synthesized starting from a wide range of chalcones in moderate to good yields with excellent diastereoselectivity.

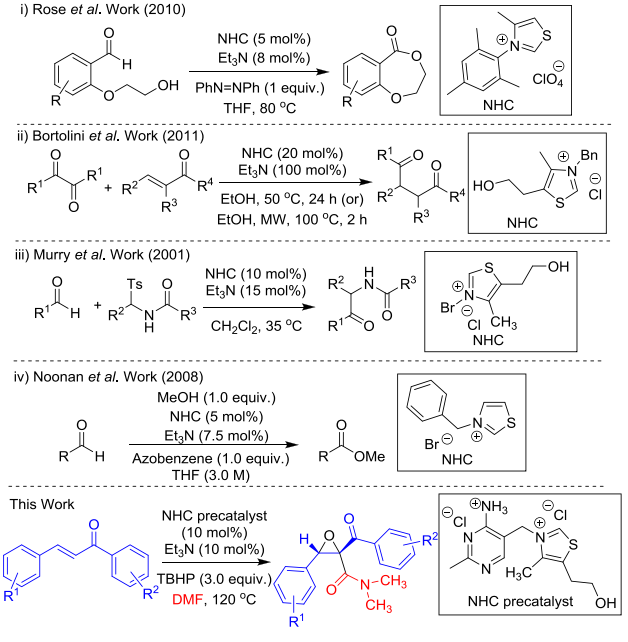


Employment of small organic molecules as catalysts, notably known as organocatalysis, gained widespread attention over the past two decades.[1] Based on their mode of binding with substrates, organocatalysts have been classified as covalent and noncovalent catalysts. Among covalent catalysts, N-Heterocyclic Carbenes (NHCs) attain greater significance due to their wide range of applicability. Even though NHCs were successfully isolated in the 1990s,[2] the seminal work of Ukai et al. in 1943 on coenzyme thiamine (vitamin B1), being used as a thiazolium based NHC catalyst for benzoin condensation reaction proved to be pioneering work in NHC catalysis.[3] The mechanism of this reaction was later proposed by Breslow which involves an acylazolium intermediate commonly known as a Breslow intermediate.[4] Since then, several chemists tried to explore thiamine as NHC for various transformations including intermolecular cross-benzoin condensation.[5] When compared with transition-metal catalysts, NHCs show low toxicity, are environmentally benign, are easy to handle, and are employed for several transformations due to their umpolung reactivity toward the carbonyl compounds.[6] Among several classes of NHCs, triazolium, imidazolium and thiazolium based N-heterocyclic carbenes acts as more prominent organocatalysts owing to their superior reactivity and wide range of transformations.[7]

Among these organocatalysts, thiazolium based NHCs gained importance due to it is historic significance and myriad synthetic applications. A few important transformations include oxidative lactonization for the synthesis of benzodioxepinone derivatives,[8a] intermolecular Stetter reaction of linear and cyclic alkyl α-diketones,[8b] synthesis of keto-amides from aldehydes and acylimines,[8c] and oxidative esterification of aldehydes[8d] (Scheme 1).

Similarly, N-heterocyclic carbene catalysis was successfully employed for the construction of *O*-heterocycles via C−O bond formation to generate phthalimides, isocoumarins, and pyrans.[9]

Scheme 1. Application of Thiazolium Derived NHCs as Organocatalysts



Likewise, various *N*-heterocycles including pyridinones, oxindoles, indole, and imidazoles were constructed via NHC

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catalyzed C−N bond formation.[10] Among, *O*-heterocycles, epoxides are privileged building blocks in organic synthesis.[11] In particular, epoxides derived from electron-deficient alkenes like *α,β*-unsaturated carbonyl compounds possess various applications in the preparation of intermediates for pharmaceutics and fine chemicals.[12] Due to their chemical importance and its myriad applications, various groups have reported the synthesis of sterically hindered epoxides, which includes Rh catalyzed synthesis of sterically hindered epoxypyrrolidines,[13a] rare earth metal amides catalyzed epoxidation of *α,β*-unsaturated ketones,[13b] TBAI catalyzed epoxidation of naphthaquinones,[13c] and Ag-NHC complex catalyzed epoxidation of diazocarbonyl compounds with aryl aldehydes.[13d] In continuation of our efforts on NHC catalyzed oxidation reaction to access compounds of biological significance,[10e,14] herein, we report the synthesis of trisubstituted epoxides bearing ketone and amide functionalities starting from various substituted chalcones and *N,N*-dimethylformamide (DMF) employing thiazolium NHC as the organocatalyst in the presence of *tert*-butyl hydroperoxide (70% aq. TBHP) as the oxidant. In the final product, the *N,N*-dimethyl formyl group was introduced and the resulting epoxide was obtained via the tandem amidation/epoxidation sequence diastereoselectively.

In order to identify the suitable reaction conditions for the synthesis of trisubstituted epoxides from chalcones and DMF, initial optimization studies were performed with chalcone **1a** as the model substrate. The role of various NHC salt precursors **A**−**K** were investigated for the formation of an epoxide, 2-benzoyl-*N,N*-dimethyl-3-phenyloxirane-2-carboxamide **2a**, employing Et_3N as base and aq. TBHP as oxidant in DMF at 120 °C (Figure 1). Among the various NHC precatalysts employed, the

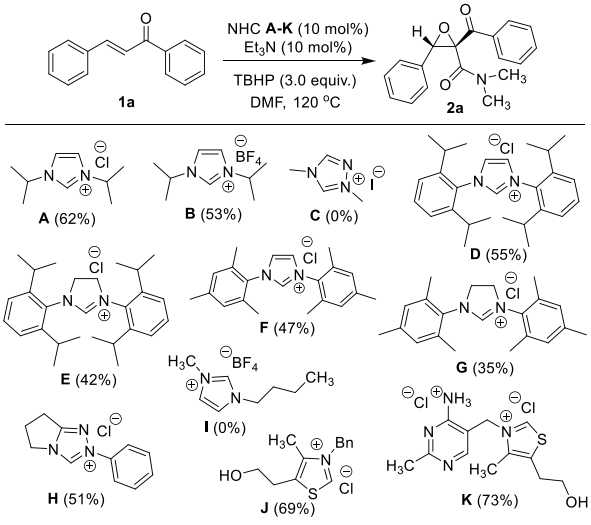
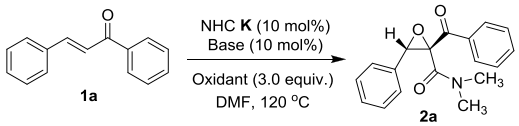


Figure 1. N-Heterocyclic carbenes used for the synthesis of trisubstituted epoxides.

yield of the desired epoxide **2a** was found to be optimum with thiazolium NHC salt precursors **J** and **K** and comparatively better yields were obtained with thiamine hydrochloride **K** as catalyst (Vitamin B_1, 73%). After identifying the suitable NHC precatalyst for this tandem amidation/epoxidation reaction, the effect of base, temperature, and oxidant were studied, and the results are summarized in Table 1.

Changing the base has a drastic effect on the product yield which was observed by varying several organic and inorganic bases in the presence of NHC precatalyst **K** at 120 °C. Among

Table 1. Optimization of the Reaction Conditions for the NHC-Catalyzed Construction of 2-Benzoyl-*N,N*-dimethyl-3-phenyloxirane-2-carboxamide[a]



Entry	Base	Oxidant	Yield (%)[b]
1	Et_3N	TBHP	73
2	*t*-BuOK	TBHP	54
3	Cs_2CO_3	TBHP	46
4	K_2CO_3	TBHP	41
5	DBU	TBHP	15
6	Piperidine	TBHP	47
7	Morpholine	TBHP	45
8	$(i\text{-Pr})_2NH$	TBHP	24
9	DIPEA	TBHP	55
10	DABCO	TBHP	23
11	Et_3N	TBHP in decane	54
12	Et_3N	Other peroxides	–[c]
13	Et_3N	TBHP	56[d]
14	Et_3N	TBHP	30[e]
15	Et_3N	TBHP	–[f]
16	Et_3N	TBHP	32[g]
17	Et_3N	TBHP	68[h]
18	Et_3N	TBHP	57[i]

[a]Reaction conditions: Chalcone **1a** (1.0 mmol), NHC precatalyst **K** (10 mol %), Base (10 mol %), Oxidant (3.0 equiv), DMF (2.0 mL), 120 °C, 1.5 h. [b]Isolated yield. [c]DTBP, DCP, BPO, TBPB, H_2O_2. [d]Reaction at 100 °C. [e]Reaction at 80 °C. [f]Reaction at rt. [g]5 mol % of base. [h]15 mol % of base. [i]2.0 equiv of oxidant.

the various inorganic bases screened (entries 2−4), *t*-BuOK was found to be the best one furnishing 54% of the epoxide. Next, several organic bases were tested (entries 1, 5−10), and among them, Et_3N produced the desired epoxide with optimal yield (entry 1). A screening of oxidants was carried out, and when TBHP in decane was used as the oxidant instead of 70% aq. TBHP, the yield of the product decreased significantly from 73% to 54% (entry 11). Other peroxides, di-*tert*-butyl peroxide (DTBP), dicumyl peroxide (DCP), benzoyl peroxide (BPO) or *tert*-butyl peroxybenzoate (TBPB) and hydrogen peroxide (30% aq. H_2O_2), did not work for this reaction (entry 12), and the effect of temperature on the product formation was also studied subsequently. It was observed that the product yield decreased when the reaction temperature was reduced from 120 °C (entries 13 and 14), and the reaction failed completely when it was performed at room temperature (entry 15). When the amount of base required to generate the free carbene was decreased from 10 mol % to 5 mol %, the yield decreased drastically from 73% to 32% (entry 16) and a further increase in the base from 10 mol % to 15 mol % did not increase the product formation (entry 17). Decreasing the oxidant from 3.0 equiv to 2.0 equiv led to a decrease in the yield of the product (entry 18). Consequently, we set entry 1 (10 mol % of NHC precatalyst **K**, 10 mol % of Et_3N, 3.0 equiv of aq. TBHP in DMF at 120 °C) as the optimized reaction conditions for further experiments.

After identifying the optimal reaction conditions, we investigated the scope and limitations of this NHC catalyzed tandem amidation/epoxidation sequence for the synthesis of trisubstituted 2-aroyl-*N,N*-dimethyl-3-aryloxirane-2-carboxamides employing various substituted *α,β*-unsaturated carbonyl

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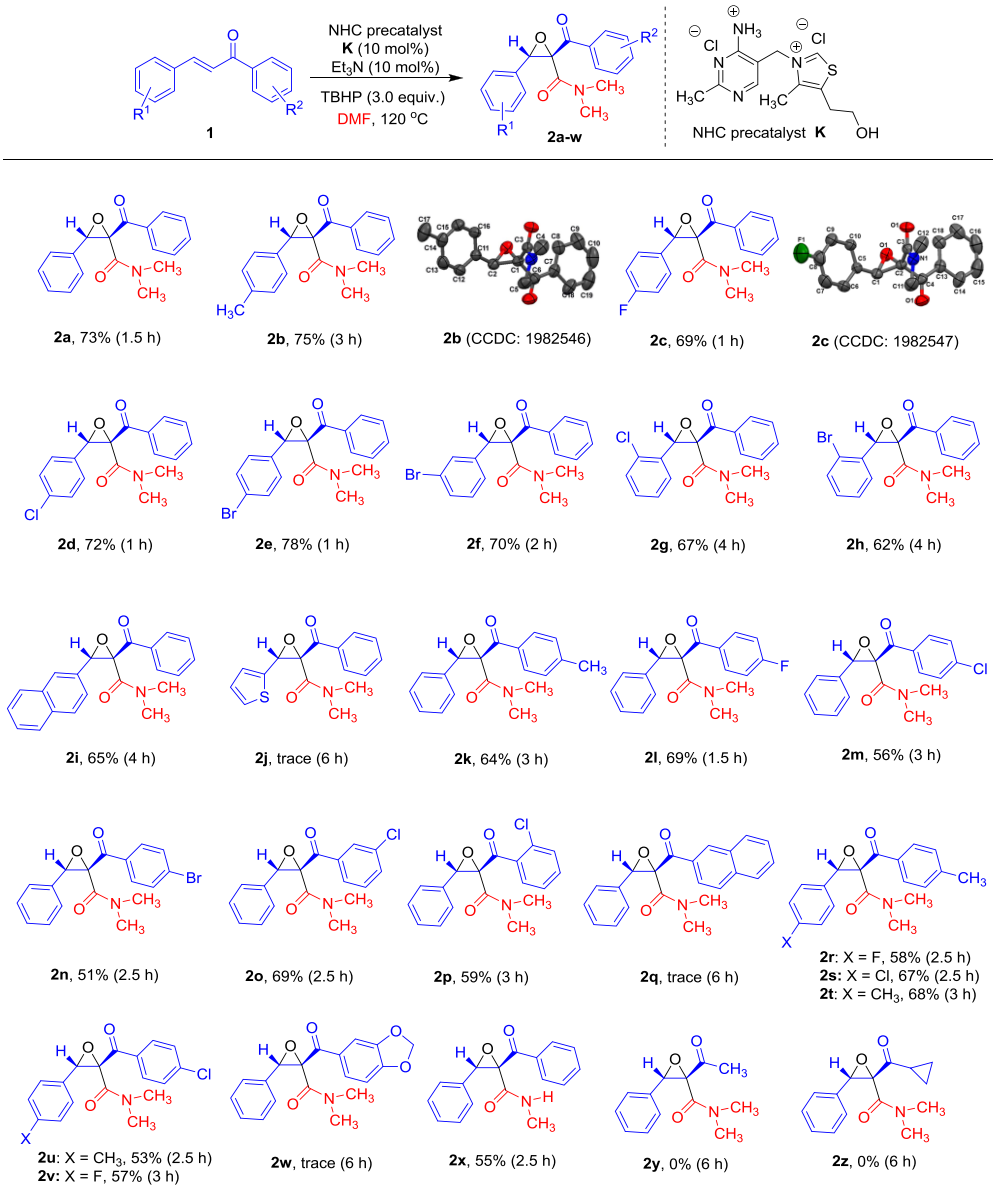
Scheme 2. Scope and Limitations for NHC Catalyzed Synthesis of 2-Aroyl-*N*,*N*-dimethyl-3-aryloxirane-2-carboxamides[a]



[a]Reaction conditions: **1** (1.0 mmol), NHC precatalyst **K** (10 mol %), Et_3N (10 mol %), aq. TBHP (3.0 equiv), DMF (2.0 mL), 120 °C. Isolated yields are reported.

compounds (Scheme 2). The reaction was tolerant to the electronic nature of substituents (R^1) at the *para* position of *α*,*β*-unsaturated carbonyl compounds, as both electron-donating and -withdrawing groups worked well to deliver the corresponding epoxides in good yields (**2b**−**e**). The steric factor had a minimal effect on this transformation, as the at *ortho* substituted (*E*)-1,3-diphenylprop-2-en-1-ones furnished the corresponding products in good yields (**2g, h**). Similarly, naphthyl substituted chalcone gave the corresponding product in good yield (65%, **2i**). The reaction of heteroaromatic (*E*)-1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one under the optimized reaction conditions furnished the corresponding product in trace amount (**2j**) even after a prolonged reaction time. When the substituent at another aryl ring (R^2) of (*E*)-1,3-diphenylprop-2-en-1-one was varied, it was observed that the position and electronic effect of the substituents have minimal effect on product yields and delivered the corresponding products in moderate to good yields (**2k**−**p**). Furthermore, reaction of (*E*)-1-(naphthalen-2-yl)-3-phenylprop-2-en-1-one under optimized conditions gave only trace amount of product **2q** after 6 h. Finally, we tested the variation at both aryl rings (R^1 and R^2) of (*E*)-1,3-diphenylprop-2-en-1-one, and the electronic nature of the substituent did not have any effect on the reaction on product yield (**2r**−**v**). When the reaction was performed with (*E*)-1-(benzo[d][1,3]dioxol-5-yl)-3-phenylprop-2-en-1-one, the corresponding epoxide was obtained in trace amount even after prolonging the reaction time (**2w**). In addition, instead of DMF, when the reaction was performed with *N*-methylformamide as solvent, the corresponding product 2-benzoyl-*N*-methyl-3-phenyloxirane-2-carboxamide **2x** was obtained in 55% yield. When the reaction was performed with *N*,*N*-dimethylacetamide, the reaction failed to deliver the corresponding product completely. Similarly, when aliphatic *α*,*β*-unsaturated carbonyl compounds like (*E*)-4-phenylbut-3-en-2-one and (*E*)-1-cyclopropyl-3-phenylprop-2-

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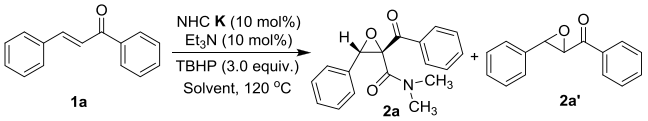
en-1-one were employed as the substrates, the reaction failed to produce the desired products **2y** and **2z**. When we extended the scope of the reaction to other aldehydes like benzaldehyde and *iso*-butyraldehyde instead of DMF, the desired epoxide was not observed.

To understand the mechanism of the NHC catalyzed tandem amidation/epoxidation sequence for the synthesis of 2-aroyl-*N,N*-dimethyl-3-aryloxirane-2-carboxamides, we carried out a set of control experiments employing chalcone **1a** as the model substrate as shown in Scheme 3. In the absence of either catalyst or oxidant, we could not observe the desired product (entries 1 and 2). In the absence of DMF as solvent and a coupling partner, there was no product formation (entry 3). From the aforesaid reactions, we can ascertain the role of catalyst, oxidant, and DMF for the formation of epoxide **2a**. When the reaction was performed with chlorobenzene, a simple epoxide, phenyl(3-phenyloxiran-2-yl)methanone **2a′**, was obtained as the major product (81%, entry 4). When epoxide **2a′** was taken as the substrate instead of **1a**, under the optimized reaction conditions, the desired product **2a** was not observed from which we can infer that the epoxide **2a′** cannot be the intermediate for the formation of **2a** (entry 5). Finally, when the reaction was carried out in the presence of 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), as radical scavenger, the desired epoxide **2a** was not observed, which confirms the existence of a radical intermediate in the catalytic cycle (entry 6).

Scheme 3. Control Experiments[a]



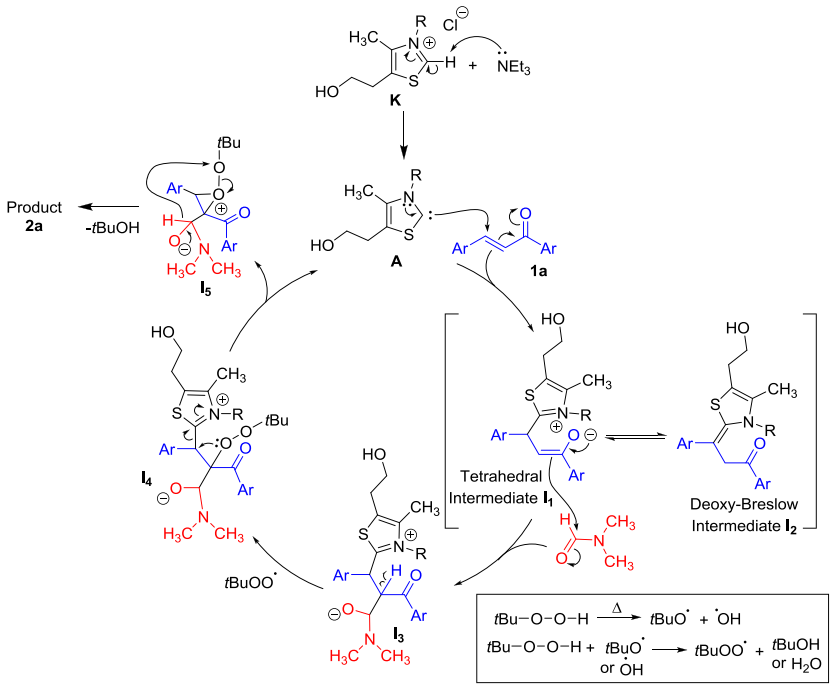
Entry	Catalyst	Solvent	Oxidant	Yield (%)[b]
1	-	DMF	TBHP	-
2	NHC	DMF	-	-
3	NHC	-	TBHP	-
4	NHC	PhCl	TBHP	-[c]
5	NHC	DMF	TBHP	-[d]
6	NHC	DMF	TBHP	-[e]

[a]Reaction conditions: **1a** (1.0 mmol), NHC precatalyst **K** (10 mol %), Et_3N (10 mol %), aq. TBHP (3.0 equiv) 120 °C, 1.5 h. [b]Isolated yield. [c]Phenyl(3-phenyloxiran-2-yl)methanone **2a′** was observed (81%). [d]**2a′** was treated with DMF under optimized condition instead of **1a**. [e]TEMPO was used as a radical scavenger.

On the basis of these control experiments, we propose a plausible mechanism for the formation of epoxide **2a** from chalcone **1a** (Scheme 4). Free carbene **A** was generated by the action of base, Et_3N, on thiamine hydrochloride **K**, which undergoes conjugate addition with **1a** to generate azolium enolate (tetrahedral intermediate) $\mathbf{I_1}$. This enolate intermediate undergoes a proton transfer to form the enamine intermediate (deoxy-Breslow intermediate) $\mathbf{I_2}$.[15] Nucleophilic attack of $\mathbf{I_1}$ on the carbonyl group of DMF generates the intermediate $\mathbf{I_3}$, where the less bulky aryl group (in comparison with NHC) and *N,N*-dimethyl formyl group were present in a sterically less hindered position (*cis*), thus accounting for the diastereoselectivity of the product formation, which was further confirmed by single crystal structures. The tertiary carbon of $\mathbf{I_3}$ can be attacked by a free radical generated from *tert*-butyl hydroperoxide (*t*BuOO$^{\cdot}$),[16] to form intermediate $\mathbf{I_4}$, which, on reorganization, generates the intermediate $\mathbf{I_5}$ along with the free carbene **A**. The trisubstituted epoxide **2a** was obtained from intermediate $\mathbf{I_5}$ via a hydride shift along with *t*-BuOH as the byproduct.

In conclusion, we have established a novel synthetic strategy for the synthesis of trisubstituted epoxides from a wide variety of chalcones and *N,N*-dimethylformamide via a tandem amidation/epoxidation sequence. The reaction takes place in the

Scheme 4. Plausible Mechanism for the Synthesis of 2a from 1a



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presence of thiamine hydrochloride as thiazolium NHC precatalyst, an environmentally benign catalyst in the presence of Et_3N as base and aq. TBHP as oxidant. This metal-free strategy was successfully employed for the synthesis of trisubstituted epoxides in moderate to good yields with excellent diastereoselectivity. Based on the control experiments, a plausible mechanism for this epoxidation was proposed which involves tandem amidation/epoxidation reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01017.

Experimental details, characterization data of compounds, NMR, and X-ray crystallographic data (PDF)

Accession Codes

CCDC 1982546−1982547 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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