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Enol Ester Synthesis via Cobalt-Catalyzed Regio- and Stereoselective Addition of Carboxylic Acids to Alkynes

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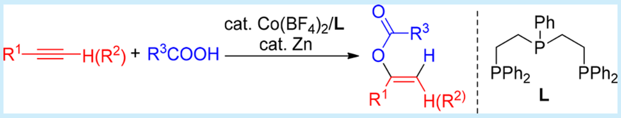
Supporting Information

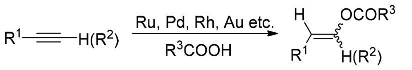
ABSTRACT: A cobalt-catalyzed highly regio- and stereoselective hydro-oxycarbonylation of alkynes is reported. Both terminal and internal alkynes can react with carboxylic acids to afford enol esters in high yields. The catalyst generated from $Co(BF_4)_2$, tridentate phosphine ligand **L5**, and zinc in situ exhibits much higher reactivity than the corresponding cobalt/diphosphine complex.



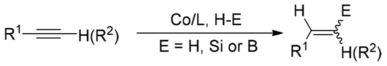
Enol esters are very versatile building blocks in organic chemistry that can be used as intermediates in polymerization, hydrogenation, and recently developed cross-coupling reactions.[1] The atom-economical addition of carboxylic acids to alkynes catalyzed by transition metals under mild conditions provides the most efficient method of preparing enol esters.[2] Although mercury salts were first used as catalysts in this transformation, their high toxicity limits its applications. Different transition metals, including Ru, Pd, Rh, Ir, Re, Au, and Ag, can be utilized in this reaction by different mechanisms and have resulted in diverse selectivities in the products (Scheme 1a).[3] However, all of these metals are expensive and unsustainable. Thus, it would be very appealing if the same products could be synthesized using earth-abundant first-row transition-metal catalysts. In the past decade, cobalt-catalyzed organic reactions have experienced significant advances.[4] Not only a simple replacement of precious metals but also better reactivities and different selectivities could also be expected. For the functionalization of alkynes, cobalt-catalyzed hydrogenation,[5] hydroboration,[6] and hydrosilylation[7] have been well-studied, in which a Co(I)−H intermediate[8] is involved and a reducing hydride reagent exists to keep the high reactivity of the cobalt catalysts (Scheme 1b). However, the addition of an acidic molecule HX to alkynes is very rare because of the decomposition of Co(I)−H in the presence of a proton.[9] Herein we report a *syn* addition of carboxylic acids to both terminal and internal alkynes catalyzed by a cobalt/triphosphine ligand complex to prepare enol esters (Scheme 1c).

Scheme 1. Transition-Metal-Catalyzed Hydrofunctionalization of Alkynes

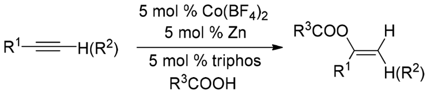
a) Precious-metal-catalyzed hydro-oxycarbonylation of alkynes



b) Cobalt-catalyzed hydro-functionalization of alkynes, Co(I)-H involved



c) Cobalt-catalyzed hydro-oxycarbonylation of alkynes, this work



Recently, the complexes of cobalt salts and tridentate ligands have exhibited especially high reactivities in different catalytic organic reactions.[10] Although different tridentate NNN, NNP, PNP, and CXC ligands have been developed for cobalt, in which two carbon atoms are always used as the linker between the coordinating atoms, the reactivity of cobalt/triphos complexes has not been well-explored (Figure 1). Elsevier and de Bruin reported the cobalt/1,1,1-tris(diphenylphosphinomethyl)ethane-catalyzed hydrogenation of carboxylic acids and esters,[11] while Beller's group realized the hydrogenation of quinoline with cobalt and a tetraphos-

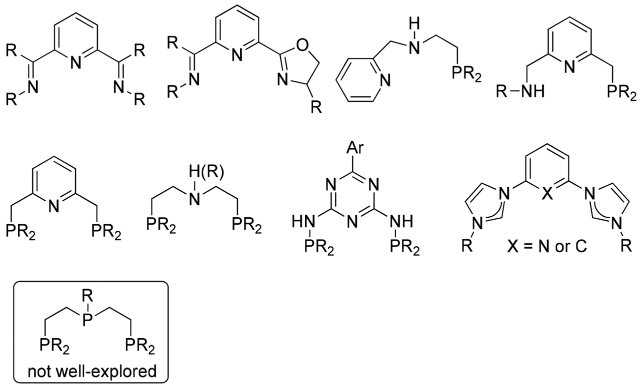


Figure 1. Selected tridentate ligands for cobalt.

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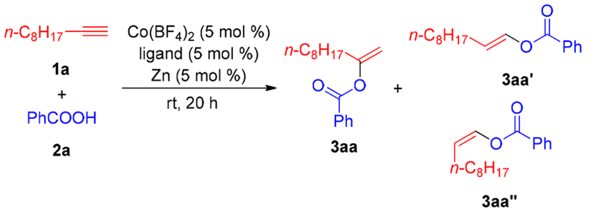
phine ligand.[12] We found that the triphos ligand bis(diphenylphosphinoethyl)phenylphosphine plays an essential role in this enol ester synthesis.

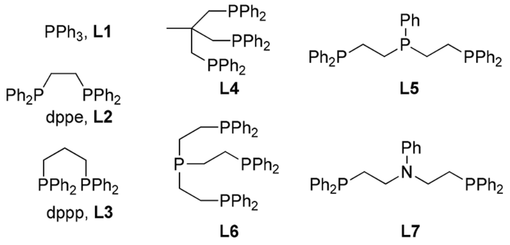
We commenced our studies with 1-decyne (**1a**) and benzoic acid (**2a**) as model substrates (Table 1). Different phosphine ligands were tested under the conditions of 5 mol % Co(BF$_4$)$_2$ and 5 mol % Zn in acetonitrile at room temperature for 20 h. With the monodentate ligand PPh$_3$ (**L1**) (entry 1), no product could be detected. Among the diphosphine ligands with different bite angles, only dppe (**L2**) and dppp (**L3**) gave low product yields and moderate regioselectivity (entries 2 and 3), while smaller- and larger-bite-angle ligands (dppm, dppb, and DPEphos) gave no products (see the Supporting Information (SI)). Furthermore, we examined the reactivities of several multiphosphorus ligands. A complex of cobalt with **L4** as the ligand showed no reactivity at all (entry 4), probably because of the long distance between the two phosphorus atoms, which does not match with the small cobalt atom. With tridentate ligand **L5**, in which there are two carbons between phosphorus atoms as in **L2**, the Markovnikov addition product **3aa** was obtained smoothly in 72% yield along with trace amounts of regiomers **3aa′** and **3aa″** (92/1) (entry 5). The extra coordination site on tetradentate ligand **L6** inhibited the same reaction (entry 6). Replacing the middle P atom by nitrogen in ligand **L7** also had a negative effect on the reactivity (entry 7), probably because of the lack of a d orbital on the nitrogen atom or the high energy of the antibonding orbital that prevents it from accepting electrons from cobalt, which suggests the key role of the middle phosphorus atom. Control reactions without cobalt salts or reducing zinc did not give any products (entries 8 and 9).

Table 1. Optimization of the Co-Catalyzed Addition of Benzoic Acid to 1-Decyne[a]



entry	catalyst	ligand	yield (%)[b]	3aa/(3aa′+3aa″)[c]
1	Co(BF$_4$)$_2$	L1	<5	–
2	Co(BF$_4$)$_2$	L2	25	3.5/1
3	Co(BF$_4$)$_2$	L3	5	3/1
4	Co(BF$_4$)$_2$	L4	<5	–
5	Co(BF$_4$)$_2$	L5	72	92/1
6	Co(BF$_4$)$_2$	L6	<5	–
7	Co(BF$_4$)$_2$	L7	<5	–
8[d]	Co(BF$_4$)$_2$	L5	<5	–
9	–	L5	<5	–
10[e]	***Co(BF$_4$)$_2$***	***L5***	***88***	***92/1***
11	Rh(cod)$_2$BF$_4$	L5	60	13/1
12[f]	[Ir(cod)Cl]$_2$	L5	<5	–

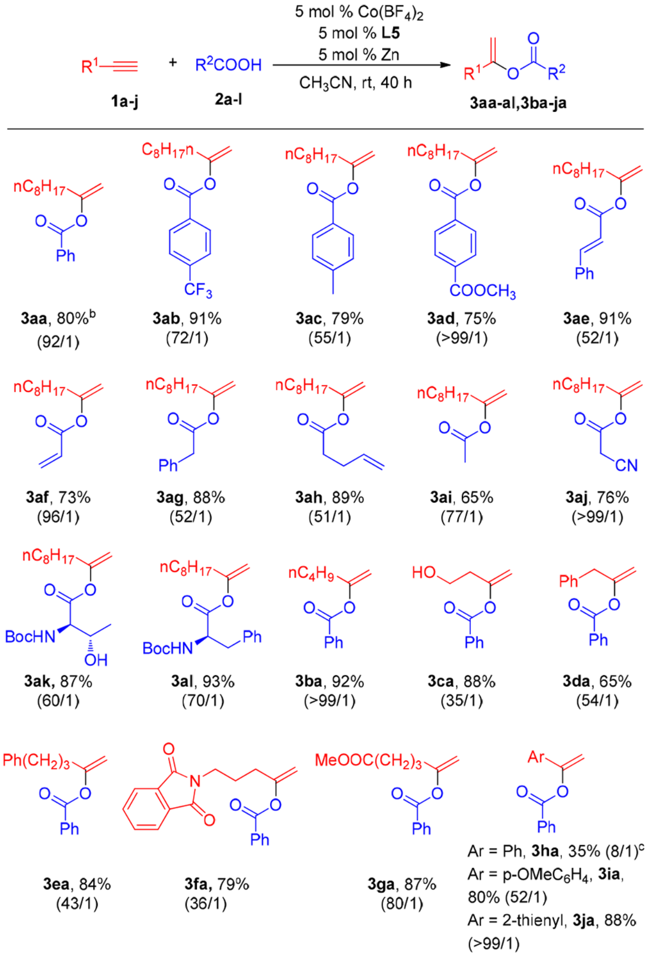
[a]Conditions: **1a** (0.5 mmol, 1.0 equiv), **2a** (0.65 mmol, 1.3 equiv), CH$_3$CN (1.5 mL). [b]Isolated yield. [c]The 3a/(3a′+3a″) ratio was determined by crude ^{1}H NMR analysis. [d]Without Zn. [e]The reaction time was 40 h. [f]2.5 mol % [Ir(cod)Cl]$_2$.



Simply extending the reaction time to 40 h resulted in higher conversion, and an 88% isolated yield was obtained (entry 10). With the same ligand **L5**, Rh(cod)$_2$BF$_4$ is less reactive and selective than cobalt, while [Ir(cod)Cl]$_2$ is inactive (entries 10 and 11). Cobalt nanoparticles were also examined, and no product was detected under the same conditions.[13] It is worth mentioning that no trimerization of terminal alkyne **1a** was observed in all cases.

With the optimized conditions in hand, we then examined the scope of the reaction (Table 2). A 10 mmol scale reaction was conducted to check the application of this reaction, and an 80% yield of **3aa** was obtained at 60 °C. Carboxylic acids with electron-withdrawing or -donating groups on the aromatic ring (**3ab**, **3ac**, and **3ad**) or carbon−carbon double bonds (**3ae**, **3af**, and **3ah**) participate in this reaction smoothly to give high

Table 2. Scope of Hydro-oxycarbonylation of Terminal Alkynes[a]

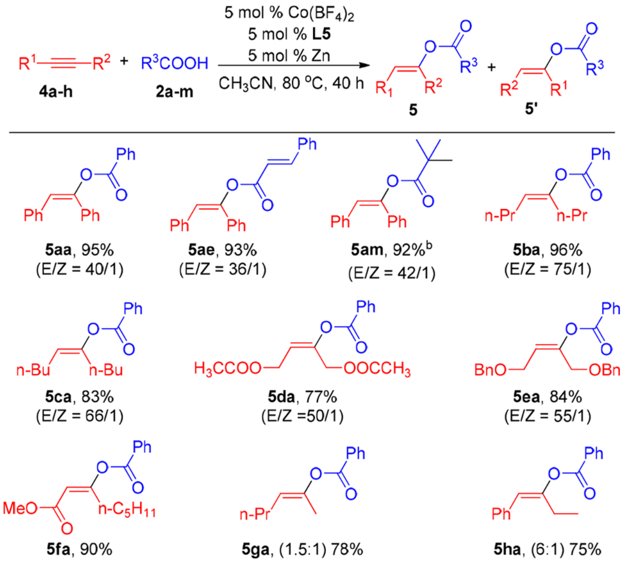


[a]Conditions: alkyne (0.5 mmol), carboxylic acid (0.65 mmol), Co(BF$_4$)$_2$ (0.025 mmol), **L5** (0.025 mmol), Zn (0.025 mmol), CH$_3$CN (1.5 mL), rt, 40 h. The ratios of isomers were determined by crude ^{1}H NMR analysis, and the yields are isolated yields. [b]10 mmol scale at 60 °C. [c]At 80 °C.

yields of products. Aliphatic carboxylic acids also work well to form enol esters (**3ag** and **3ai**). Different functional groups (cyano, free hydroxyl, and amide) in the acids do not affect the reaction (**3aj**, **3ak**, and **3al**). On the other side, functionalized terminal alkynes were tested. A phenyl ring, free hydroxyl group, protected amine, and ester can all be tolerated in this reaction (**3ba** to **3ga**). Besides aliphatic alkynes, aromatic alkynes were also evaluated. When phenylacetylene was added to the reaction, only a 35% yield of the product (**3ha**) was obtained, along with the enyne generated by homocoupling of the terminal alkyne. We assume that the more acidic aromatic alkynes can have an exchange reaction with the carboxylate intermediate. This assumption was proven by applying less acidic substrates, as **3ia** and **3ja** were isolated in 80% and 88% yield, respectively.

Encouraged by the cobalt-catalyzed addition of carboxylic acids to terminal alkynes, we further investigated whether more challenging internal alkynes can also work in this reaction (Table 3).[14] Under the same reaction conditions, no product was detected. However, when the temperature was increased to 80 °C, **5aa**, the addition product from diphenylacetylene (**4a**), was obtained in 95% yield with exclusive *syn* selectivity. To the best of our knowledge, only two Ru complexes can catalyze the formation of (*E*)-enol esters by *syn* hydro-oxycarbonylation of internal alkynes.[13] Cinnamic acid and pivalic acid also reacted, giving **5ae** and **5am**, respectively, in high yields. Symmetric aliphatic internal alkynes also easily reacted to form **5ba** to **5ea**. Compound **5fa** was generated with exclusive addition of the acid to the electropositive *β*-position, which is controlled by the electron distribution on the alkyne. Asymmetric 2-hexyne afforded the products **5ga** and **5ga′** without good regioselectivity, while phenylethylacetylene (**4h**) reacted to give a 6/1 ratio favoring **5ha**. The high reactivity of internal alkynes can also help exclude the possible mechanism involving metal vinylidenes.[15]

Table 3. Scope of Hydro-oxycarbonylation of Internal Alkynes[a]



[a]Conditions: alkyne (0.5 mmol), carboxylic acid (0.65 mmol), Co(BF$_4$)$_2$ (0.025 mmol), **L5** (0.025 mmol), Zn (0.025 mmol), CH$_3$CN (1.5 mL), 80 °C, 40 h. The ratios of the isomers were determined by crude ^{1}H NMR analysis, and the yields are isolated yields. The product configuration was confirmed by previous reports. [b]At 100 °C.

Tridentate phosphine ligand **L5** exhibits much higher reactivity than diphosphines. Its cobalt complex CoCl$_2$·**L5** can be easily prepared by mixing CoCl$_2$ and **L5** in dichloromethane. The crystal structure reveals that all three phosphorus atoms coordinate to the cobalt center (Figure 2 left). The crystal geometry is distorted square-pyramidal, and the τ_5 value is 0.20 (the two greatest bond angles are 165.60° for P1−Co−P3 and 153.34° for P2−Co−Cl2). The CoCl$_2$·**L5** complex itself is not active in this addition reaction. Upon reduction with Zn, the Markovnikov addition product **3aa** was obtained in 92% yield.

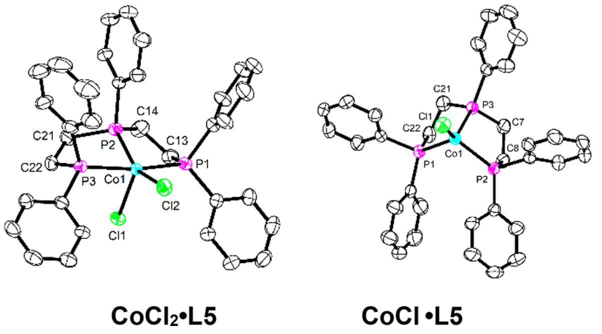
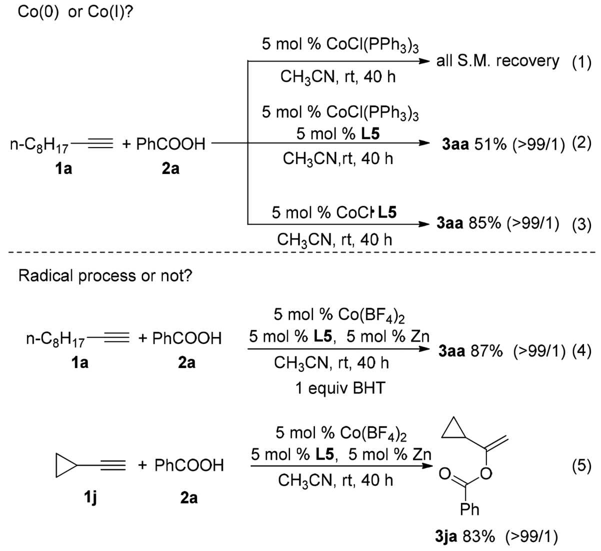


Figure 2. Structures of CoCl$_2$·**L5** and CoCl·**L5**.

Control experiments were conducted to address two questions for the mechanism (Scheme 2): (1) Is the reaction catalyzed by a Co(0) or Co(I) complex?[16] (2) Is a radical process involved in this addition reaction? When 5 mol % CoCl(PPh$_3$)$_3$[17] was used in this reaction, both substrates **1a** and **2a** were recovered (eq 1). However, the addition of 5 mol % **L5** led to the formation of **3aa** in 51% yield (eq 2). These results suggest that triphos ligand **L5** replaces PPh$_3$ and that an active Co(I) complex catalyzes the addition reaction. CoCl·**L5** was prepared by mixing CoCl$_2$, **L5**, and NaBH$_4$ in EtOH. The crystal structure was obtained (Figure 2 right), showing that the complex adopts a distorted tetrahedral geometry with τ_4 = 0.78 (the two greatest bond angles are 125.56° for P3−Co−Cl

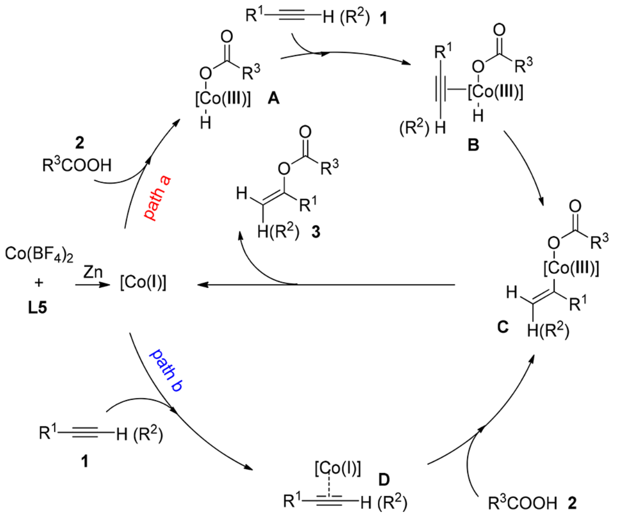
Scheme 2. Mechanistic Studies



and 124.45° for P2−Co−Cl). CoCl·**L5** exhibits similar efficiency as the in situ-generated Co(I) catalyst, giving an 85% yield under the standard conditions (eq 3). This result further supports that triphos/Co(I) complex is able to catalyze the addition reaction. For the second question, 1 equiv of the radical scavenger BHT was added to the standard conditions, and no inhibition effect was observed (eq 4). Furthermore, cyclopropyl alkyne **1k** was tested as a radical clock (eq 5). The normal addition product **3ka** was isolated in 83% yield, and no allene was detected (see the SI).[18] These two reactions support our hypothesis that a vinyl radial intermediate is probably not involved in the catalysis.

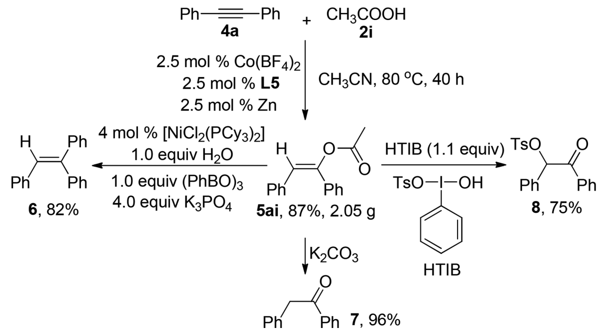
On the basis of the above experiments and literature reports, we proposed two plausible mechanisms (Scheme 3). The cobalt(II)/**L5** complex is reduced in situ by zinc to form a reactive [Co(I)] catalyst. In path a, [Co(I)] can undergo oxidative addition with carboxylic acid **2** to generate Co(III) intermediate **A**. This mechanism was proposed in the iridium-catalyzed reactions of carboxylic acids and supported by the isolation of an Ir(III)−H complex.[19] Coordination of A with alkyne **1** forms **B**, and subsequent migratory insertion in **B** leads to intermediate **C**. Direct reductive elimination from **C** releases the product enol ester **3** and regenerates the Co(I) catalyst. In path b, [Co(I)] coordinates with alkyne **1** to form Co(I) complex **D**. Oxidative addition of complex **D** with carboxylic acid **2** forms the same vinyl Co(III) carboxylate **C**. Stoichiometric rhodium chemistry by Wolf and Werner[20a] and rhenium chemistry by Casey et al.[20b] gave the precedents. A similar mechanism was proposed and calculated by the Breit group in the catalytic reaction by rhodium, in which the barrier for intramolecular protonation was lower than that in path a.[20c] CpCo/alkyne complexes can also be synthesized from Co(I) and alkynes.[21] A stoichiometric reaction of CoCl·**L5** and benzoic acid was conducted to check the possibility of path a. However, none of the new species was observed by ^{1}H NMR spectroscopy (see the SI). This result may suggest that intermediate **A** is not formed without the help of the alkyne. Although no Co/alkyne intermediate was isolated directly, path b is more likely because CoCl·**L5** is able to catalyze the homocoupling of phenylacetylene (**1h**) in 75% yield at room temperature without carboxylic acids, in which one molecule of acidic phenylacetylene may take the place of benzoic acid.

Scheme 3. Proposed Mechanism



The cobalt-catalyzed addition of carboxylic acids to alkynes can be used for the gram-scale synthesis of enol esters (Scheme 4). Two grams of compound **5ai** was obtained in 87% yield from **4a** and **2a** under the catalysis of 2.5 mol % cobalt at 80 °C. The enol ester **5ai** could be transformed into triphenylethene (**6**) via a nickel-catalyzed cross-coupling reaction.[22] Ketones **7** and **8** were obtained smoothly under hydrolysis and oxidation conditions, respectively.[23]

Scheme 4. Gram-Scale Synthesis and Transformations of Enol Ester 5ai



In summary, we have reported a practical cobalt/triphos-catalyzed method for the synthesis of enol esters from carboxylic acids and alkynes in high yield with high stereoselectivity. Both the cobalt salt and the ligand are commercially available and nonexpensive. This is another example that earth-abundant first-row transition metals can take the place of precious late transition metals. The use of tridentate phosphorus ligand **L5**[24] is essential for the reactivity of the cobalt catalysis. Further applications of the cobalt/triphos complex are under investigation in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02824.

> Detailed experimental procedures, characterization data, copies of ^{1}H and ^{13}C NMR spectra, and X-ray crystal structures of CoCl$_2$·**L5** and CoCl·**L5** (PDF)

Accession Codes

CCDC 1826753 and 1865904 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 e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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