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Preparation of a Rigid and Nearly Coplanar Bis-tetracene Dimer through an Application of the CANAL Reaction

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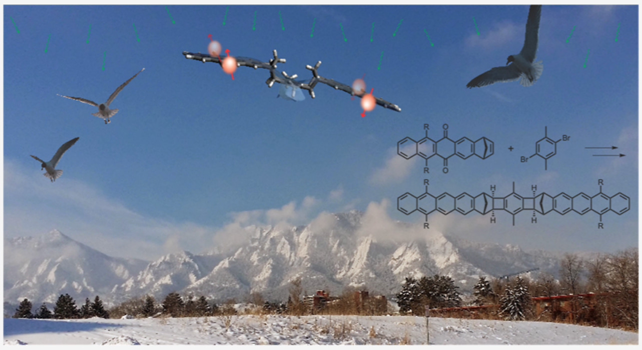
ABSTRACT: A rigid tetracene dimer with a substantial interchromophore distance has been prepared through an application of the recently developed catalytic arene-norbornene annulation (CANAL) reaction. An iterative cycloaddition route was found to be unsuccessful, so a shorter route was adopted whereby fragments were coupled in the penultimate step to form a 13:1 mixture of two diastereomers, the major of which was isolated and crystallized. Constituent tetracene moieties are linked with a rigid, well-defined bridge and feature a near-co-planar mutual orientation of the acenes.



■ INTRODUCTION

Anthropogenic climate change has fueled research in next-generation solar energy conversion technologies, including ones aiming to bypass the Shockley−Queisser limit, the theoretical ceiling on the power-conversion efficiency of single-junction solar cells.[1,2] A centerpiece of these efforts is the study of singlet fission (SF), a phenomenon of energetic proportionation between an excited-state chromophore and a ground-state neighbor.[3] The SF reaction originates in a single chromophore, or a material-extended singlet-excitonexcited state that is generally the lowest energy S_1. The reaction culminates in the formation of independent triplets on separate chromophores, first passing through a multiexcitonic state consisting of two triplets coupled into a net singlet (^{1}TT). It is the study of factors controlling $S_1 \rightarrow {}^1$TT dynamics that led us and others to consider molecular dimers as fundamental platforms where reaction parameters such as driving force and interchromophore electronic coupling could be systematically varied, drawing on a vast toolbox of organic synthesis to control both bridge and chromophore type and the nature of connectivity.[4−13] A central theme in our efforts has been the consideration of structurally well-defined acene dimers using bicyclic alkyl bridging units derived from norbornadiene[14−18] including synthesis-specific work.[15,17]

Recently, it has been realized that dynamics at play in the initial steps of SF may have value well beyond solar technologies, reaching into quantum information sciences.[19−22] In that field, qubits (quantum bits) are needed for computation or sensing, requiring the initialization of quantum-mechanically pure states, commonly based on spin angular momentum.[23] In order to avoid the need for exceedingly low temperatures for qubit initialization, there is great interest in identifying systems where optical excitation is coupled with spin selectivity in the dynamics, resulting in the generation of pure states.[24−26] The reason that SF becomes interesting in this context lies in opportunities to exploit spin dynamics in the multiexciton manifold—that includes ^{1}TT but also states with ^{5}TT and ^{3}TT characters—to selectively focus excited-state population into specific magnetic sublevels such as the ^{5}TT$_0$.[19] We have recently shown this to be the case in a rigid norbornyl-bridged TIPS-pentacene dimer (TIPS-BP1′) at elevated temperature (90 K) and have demonstrated relatively long T_2 times reflecting coherence between ^{5}TT$_0$ and ^{5}TT$_{\pm1}$ states.[22] More specifically tied to the synthetic goals in this paper, it has recently been predicted that when two chromophores share a common set of axes relative to an external magnetic field—in other words, when they are parallel—selection rules are imposed such that dynamics leading to the loss of the ^{5}TT$_0$ to other states in the manifold will be slowed.[19] These are conditions that could increase the time needed to perform qubit operations.

As alluded to above, our groups have been interested in the synthesis and study of rigid acene dimers, and we have previously utilized [2.2.1] bicyclic bridges that impose structural definition via two covalent points of attachment between the bridge and each chromophore. A computational

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model of an acetylene-substituted pentacene dimer (BP1′) leads to a prediction of 111° for the interchromophore angle, a significant deviation from coplanarity [Figure 1 (top) and a related tetracene system[14]]. As a follow up to these studies, we have targeted extended ("X") tetracene and pentacene analogues of BT1′ and BP1′ [TIPS-BTX and TIPS-BPX, respectively, Figure 1 (bottom)]. In these structures, the acene chromophores are fused to norbornyl groups via cyclobutenyl bridging units connected by a central aryl group. The cyclobutenyl groups ensure a rigid core, and the fusion with the norbornyl groups stabilizes this functionality to ring opening,[27] which would result in an anti-Bredt olefin. There are two diastereomers of the dimers that are observed via our synthesis (vide infra), wherein the constituent chromophores are *syn*- or *anti*-. Computational models of pentacene versions—again with acetylene substituents—are shown in Figure 1 (top, *syn*-BPX and *anti*-BPX). In both isomers, the chromophores are predicted to have a much higher degree of coplanarity, with an interchromophore angle of 179.5° for the *anti*-isomer, and 166.5° for the *syn*-isomer. Although both isomers have the desired near-coplanar arrangement of chromophores, a mixture would introduce complexity in future interpretations of excited state dynamics and spin dynamics, and it is therefore important to prepare and isolate these compounds as single diastereomers, not mixtures. In this manuscript, we discuss the synthesis of TIPS-BTX and our initial unsuccessful approach to TIPS-BPX. We will report on the synthesis of TIPS-BPX shortly. An initial report of the synthesis of TIPS-BTX was made on ChemRxiv.[28]

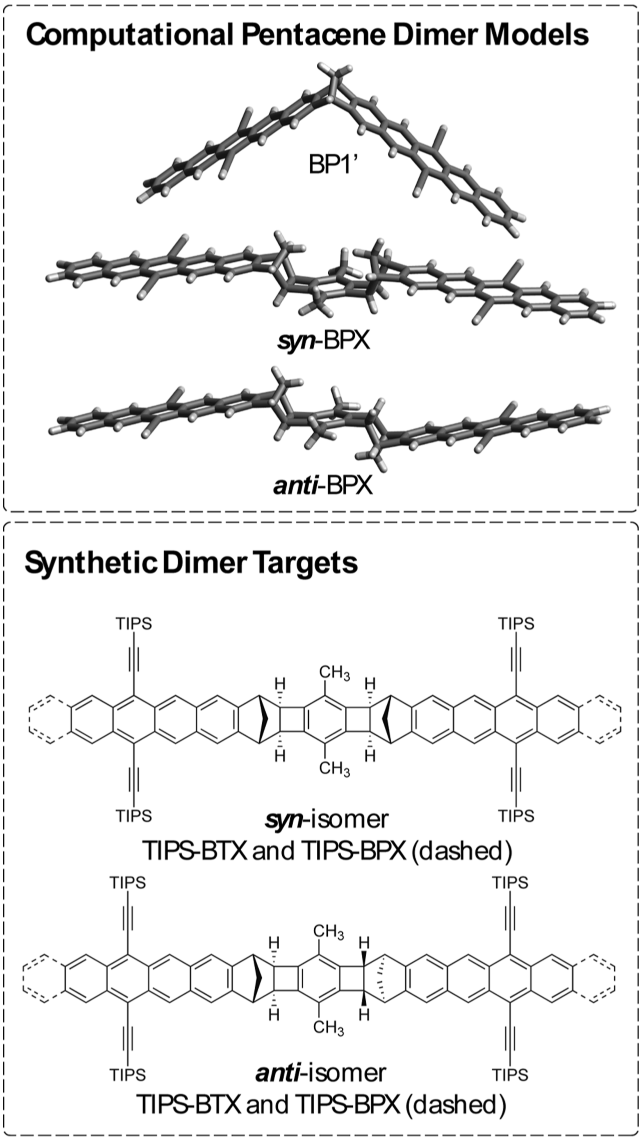


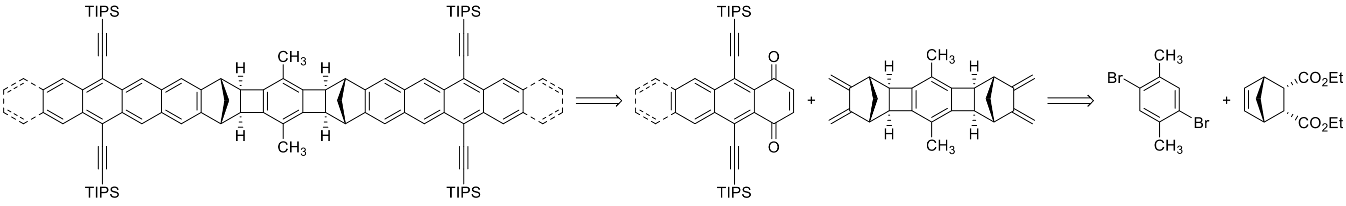
Figure 1. (Top) Computational models of acetylene-substituted pentacene dimers. Density functional theory was used with the ωB97X-D density functional, the 6-31G(d) basis set, and a polarizable continuum model of solvent parameterized for toluene. The calculated interchromophore angle of BP1′ is 111.4°, *syn*-BPX is 166.5°, and *anti*-BPX is 179.5°. (Bottom) Dimeric targets TIPS-BTX and TIPS-BPX (dashed bonds), with both possible isomers *syn* and *anti* shown.

■ RESULTS AND DISCUSSION

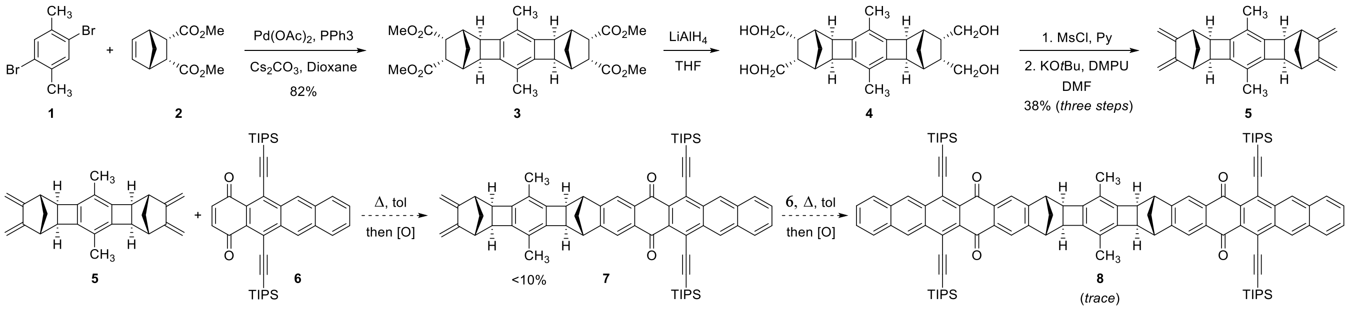
Initial Synthetic Approach. Our initial retrosynthetic analysis of TIPS-BPX drew from our experience with the synthesis of TIPS-BP1′[17] and is shown in Scheme 1. As in the case of our prior synthesis, we wished to employ a 2-directional Diels–Alder approach between a bis-diene in the central portion of the molecule and a quinone dienophile. Ideally, this would be a one-pot, double-Diels–Alder reaction, though a sequential approach as was employed in our synthesis of TIPS-BP1′ was considered as a backup. In either case, the product of the Diels–Alder reaction would be subjected to a sequence consisting of oxidative aromatization (O_2/Al_2O_3) of the cycloadduct, followed by reduction of the quinone ($NaBH_4$) to the corresponding diol, and a final reductive aromatization ($SnCl_2$) to provide the bis-acene.

We adopted a transform-goal approach to the synthesis of bis-diene **5** (Scheme 2) using the catalytic arene-norbornene annulation (CANAL) reaction developed by Xia[29] for the construction of the cyclobutenyl fragments. The CANAL transformation typically employs a bromo-arene, wherein one of the sites *ortho*- to the bromine is blocked to direct reactivity to the other site. As such, we chose the di-bromo *p*-xylene derivative **1** as our starting material, which we subjected to the CANAL reaction with norbornene bis-ester **2** [$Pd(OAc)_2/PPh_3/Cs_2CO_3$, 82%] to provide tetraester **3** as a 4:1 mixture of

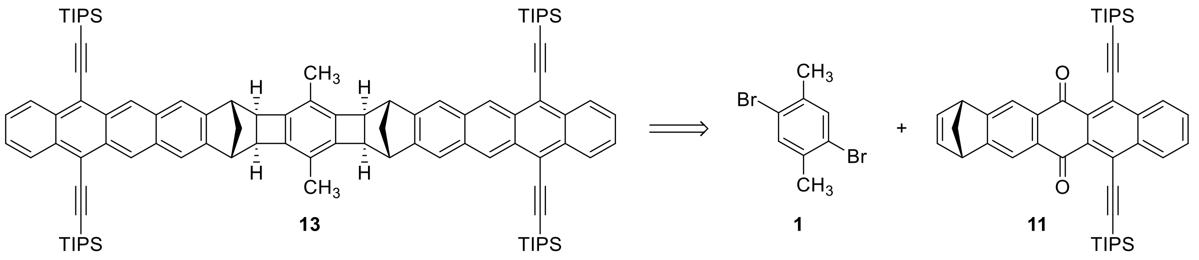
Scheme 1. Initial Retrosynthesis of TIPS-BTX and TIPS-BPX (Dashed Bonds)



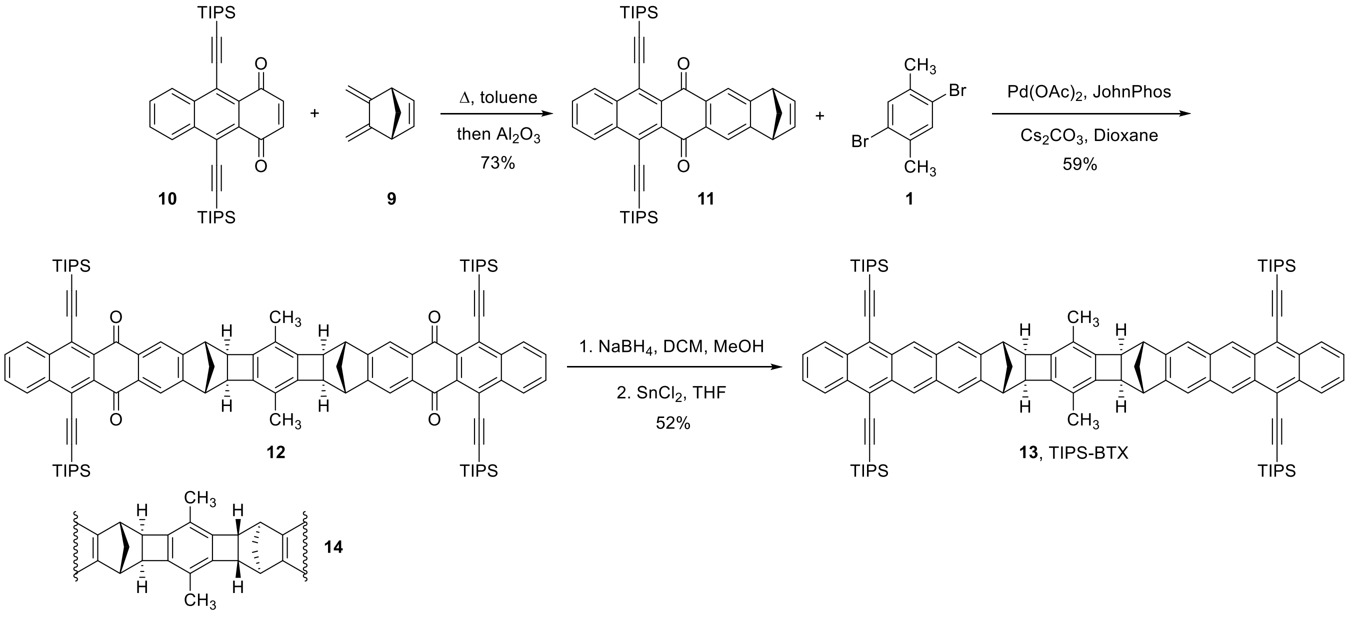
Scheme 2. Initial Approach to TIPS-BPX



Scheme 3. Retrosynthesis of TIPS-BTX (Only *Syn*-isomer Shown)



Scheme 4. Synthesis of TIPS-BTX



two *exo*-stereoisomers, wherein the norbornyl methylenes are located on either the same or the opposite face of the molecule. The stereochemical assignment depicted in Scheme 2 for the major isomer was made in analogy to the observed stereochemistry in subsequent CANAL reactions (vide infra). LAH reduction of **3** provides the corresponding tetraol **4** with poor solubility in a variety of solvents, limiting our ability to purify it by chromatography. As such, it was taken on crude to the tetra mesylate (MsCl/Py), which similarly displayed poor solubility in common chromatographic solvents, and was subjected to elimination (*t*-BuOK/DMPU/DMF) without purification. By this three-step sequence, compound **5** was obtained in a 38% overall yield from **3** after purification by flash chromatography.

Bis-diene **5** was next subjected to a Diels–Alder cycloaddition (75 °C) with a single equivalent[30] of quinone dienophile **6**, the synthesis of which we have previously described.[17] The reaction is conducted solvent-free under nitrogen, and the crude ^{1}H NMR spectrum shows clean and essentially complete conversion to the single addition product, with none of the bis-cycloaddition product detected.[31] This crude material was subjected to aromatization to compound **7** using protocols known to be effective in our synthesis of TIPS-BP1′. These conditions consist of subjection to basic alumina in toluene with rapid stirring and exposure to air. While this procedure is effective for the synthesis of a variety of norbornyl-bridged acene quinones, here it provides mostly decomposed material with a small quantity of the desired aromatized cycloadduct. Other aromatization reagents and conditions were studied on related systems without success. These include the use of silica (no reaction at RT); alumina embedded with potassium permanganate[32] (decomposition of the starting material with no product recovered at temperatures as low as −32 °C); and DDQ or *p*-chloranil (no reaction at room temperature, cycloaddition with the terminal diene, with no desired dehydrogenation observed at elevated temperature). Though we had limited supplies of compound **7** that were not homogeneous, we pushed our synthesis forward with the amounts we were able to produce from the alumina oxidation conditions. Subjection of **7** to Diels−Alder cycloaddition with quinone **6** was performed using conditions akin to the first cycloaddition (neat, 90 °C) and similarly produced cycloadduct in essentially quantitative mass balance. Unfortunately, aromatization of the Diels−Alder product to **8** again proved problematic, with no conditions providing usable amounts of material.

The reticence of these Diels−Alder cycloadducts to undergo oxidative aromatization to compounds **7** and **8** in comparison to our previous studies suggests that the cyclobutene moieties play a detrimental role, providing a pathway for decomposition in preference to aromatization.[33,34] We note that these moieties are not present in the successful oxidative aromatization reactions required for the synthesis of TIPS-BT1′ and TIPS-BP1′, and we speculate that cyclobutyl carbinyl radical species are formed in the aromatization pathway and that these undergo fragmentation to provide complex mixtures of products.[15,17]

BTX: A Second Target and Approach. Given the challenges discussed above for TIPS-BPX, a revised strategy was pursued and explored in the synthesis of a tetracene dimer analogue (TIPS-B*T*X, as opposed to TIPS-B*P*X). We chose the tetracene variant because, in our experience, the synthesis of tetracene derivatives proceeds more smoothly than that of analogous pentacenic molecules. Our approach was still transform-goal-driven with the use of the CANAL reaction to construct the cyclobutenyl rings, but we wished to employ this transformation later in the synthesis after application of the oxidative aromatization, which is problematic in the presence of the cyclobutenyl groups. Our retrosynthetic disconnection is shown in Scheme 3 and proceeds via dibromide **1** and norbornene **11**. Application of the CANAL reaction to these substrates would give a bis-quinone product that, upon reductive aromatization, would provide the target dimer TIPS-BTX.

In the forward direction (Scheme 4), our synthesis begins with the known[35] triene **9**, the preparation of which can be accomplished in two steps from cyclopentadiene. Subjecting **9** to a Diels−Alder reaction with dienophile **10**[17] followed by aromatization (alumina/air, RT) provides cycloadduct **11** in 73% yield without the decomposition issues observed in the preparation of **7**. Our initial attempts at application of the CANAL reaction of dibromo-*p*-xylene derivative **1** with olefin **11**, a much larger coupling partner than its analogue (**2**) in our initial synthesis, yielded primarily the mono-coupling product (17% yield) with a small quantity of the desired bisquinone (**12**, 8% yield). Fortunately, the use of JohnPhos in place of triphenylphosphine [$Pd(OAc)_2$/JohnPhos[36,37]/Cs_2CO_3] provided bis-quinone **12** in 59% yield, with little observed mono-coupling product. Similar trends in reactivity have been observed by Xia.[36,37]

This transformation, which is the penultimate step of the synthesis, can, in principle, provide up to 6 diastereomers, but because of the high *exo*-selectivity of the CANAL reaction,[29,37] only two diastereomers are formed. Interestingly, these are produced in a 13:1 ratio and are separable by flash chromatography. The major isomer was crystallized from toluene, and its was structure determined by X-ray crystallography (Figure 2). This was found to be the *syn*-bis-tetracene-quinone (**12**), with the *anti*-bis-tetracene-quinone (**14**) as the minor diastereomer. Remarkable in this transformation are not only the levels of remote stereoselection, but also that the seemingly contra-steric product, with the two norbornyl methylenes on the same side of the molecule, is major.

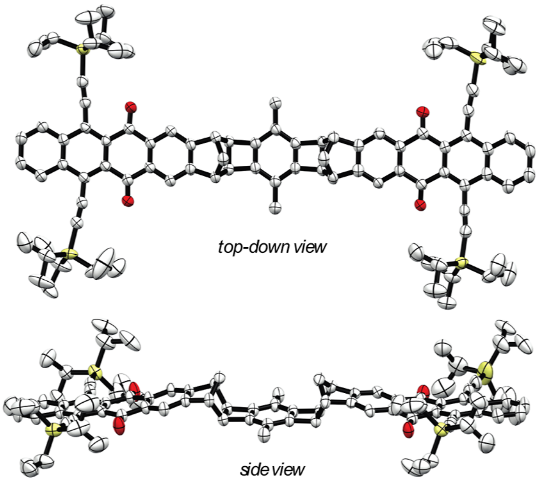


Figure 2. Crystal structure of *syn*-bis-tetracene-quinone **12** from two perspectives with thermal ellipsoids rendered at 50% probability. C = white, O = red, and Si = yellow. Hydrogen atoms have been removed for clarity. As described in the Supporting Information but not shown here (again for clarity), there are ∼4 disordered toluene solvent molecules as well as disorder in two of the four TIPS substituents.

Reduction of *syn*-bis-tetracene-quinone **12** ($NaBH_4$/DCM/MeOH) provides tetraol intermediates, which were isolated then subjected without purification to reductive aromatization ($SnCl_2$/THF) to provide the acene dimer TIPS-BTX (**13**) in 52% yield. We note an improvement in this reaction using this process (wherein we isolate the crude tetraol) vs our previous one-pot approach and speculate that this is due to the superior solubility of stannous chloride in THF as opposed to the mixed solvent system of the one-pot procedure. The final target (**13**, TIPS-BTX) is sensitive to untreated silica but not to silica deactivated by prior washing with triethylamine. We speculate that the acidity of silica promotes decomposition via protonation of the acene concomitant with the opening of the cyclobutyl moiety.

This synthesis illustrates the use of the CANAL reaction for the preparation of novel acene dimers. Our transition from a longer, iterative cycloaddition strategy to a two-directional/one-pot strategy not only shortens the synthesis but also highlights the importance of considering functional group sensitivity in synthetic planning. An important lesson learned from this work is that consideration of the timing of the oxidative aromatization in conjunction with the CANAL reaction avoids the formation of undesired side-products due to the presence of sensitive moieties. This work also demonstrates the scope and limitations of the CANAL reaction. The synthetic strategies developed herein are being employed and expanded upon to generate other acene-derived analogues of TIPS-BTX to study the dynamics of multiexciton states.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article, its Supporting Information, and the CCDC for the crystal structure cif and related files.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.3c00809.

Reaction details, NMR data, and X-ray diffraction experiment details (PDF)

Accession Codes

CCDC 2255193 contains 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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