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Intermolecular Oxidative Friedel–Crafts Reaction Triggered Ring Expansion Affording 9,10-Diarylphenanthrenes

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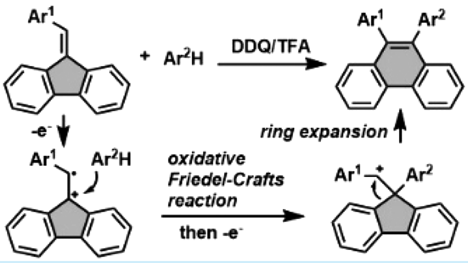
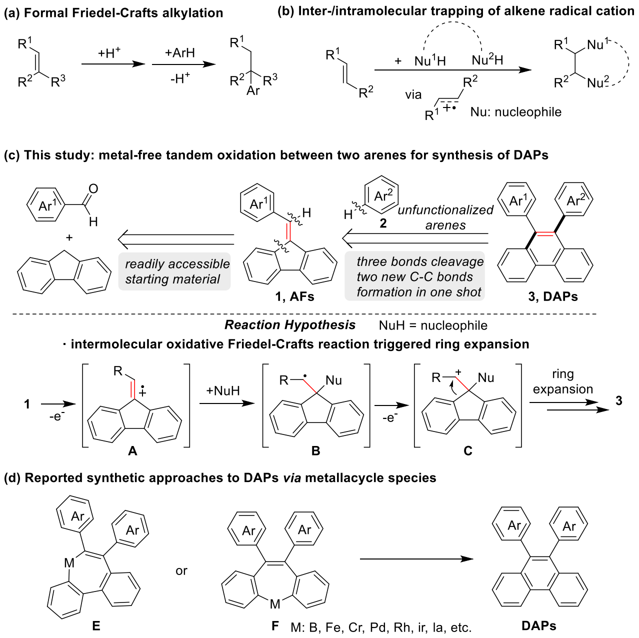
ABSTRACT: A novel intermolecular tandem oxidative aromatic coupling between arylidene fluorenes and unfunctionalized aromatics mediated by a DDQ/TFA oxidation system has been developed for the construction of 9,10-diarylphenanthrenes (DAPs). The formation of a benzylic carbocation species possessing a quaternary sp^3-carbon center on the fluorene moiety by an intermolecular oxidative Friedel–Crafts reaction of two different arenes successfully triggered the subsequent ring expansion to afford DAPs.



Among a variety of synthetic methods toward polycyclic aromatic hydrocarbons (PAH),[1,2] the intramolecular oxidative aromatic coupling of the precisely preconstructed multiaryl-substituted arenes using various single electron oxidants has been considered as one of the most straightforward and atom-economical synthetic strategies.[2] On the other hand, the intermolecular oxidative aromatic cross-coupling between two different arenes having inequivalent reactive sites typically produced unsymmetrical biaryls sometimes accompanied by homocoupling side reactions.[2b] Consequently, the development of a novel version of the intermolecular oxidation reaction between different arenes toward PAHs by suppressing the potential formation of the undesired cross-coupling and homocoupling products is highly desirable and challenging. The Friedel–Crafts alkylation reaction is one of the most important methods for C–C bond formation (Scheme 1a).[3] Meanwhile, functionalization of alkene by intermolecular and intramolecular trapping of radical cations was also developed (Scheme 1b).[4] In this work, we have developed an intermolecular oxidative Friedel–Crafts reaction triggered ring expansion tandem process through the formation of an all-carbon quaternary center carbocation for constructing PAH products (Scheme 1c). This successive loss of two electrons, followed by rearrangement to achieve aromatic compounds, has been rarely reported.

Scheme 1. Development of New Intermolecular Oxidative Coupling of Arenes for Synthesis of DAPs


(a) Formal Friedel-Crafts alkylation

(b) Inter-/intramolecular trapping of alkene radical cation

(c) This study: metal-free tandem oxidation between two arenes for synthesis of DAPs

(d) Reported synthetic approaches to DAPs *via* metallacycle species

Recently, we have been interested in developing new intramolecular single electron oxidative tandem annulations toward the synthesis of structurally diverse π-extended polycycles.[5] We have found that the formation of a radical cation species at the alkenyl moiety of arylidene fluorenes was considered to be a key feature to induce the subsequent spirocyclization and ring expansion processes. In light of our previous studies,[5] we assumed that if a single electron oxidation occurs at the alkenyl moiety of arylidene fluorenes (**1**, AF), the resulting radical cation species **A** may induce subsequent intermolecular oxidative Friedel–Crafts reaction with aromatic nucleophiles, followed by a ring expansion reaction through 1,2-

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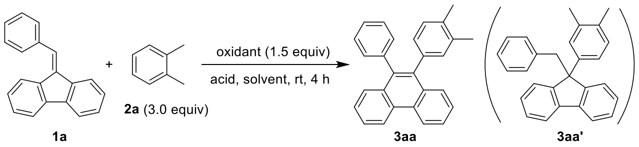
aryl shift in the intermediate **C**, leading to 1,2-diarylphenanthrenes (**3**, DAPs) (Scheme 1c). However, under the single electron oxidation conditions, some potential compete side-reactions were considered to occur in our reaction hypothesis. For example, (a) typical homocouplings and cross-couplings of two arenes,[2b] (b) intramolecular cyclodehydrogenative coupling of the intermediate **A** (R = Ar^1),[6] (c) 1,2-aryl shift of the nucleophilic aromatic group (Nu) in the intermediate **C** (vide infra; see Scheme 5b, presented later in this work), and (d) formal intermolecular Friedel–Crafts reaction, may erode the desired reaction efficiency.

As one of the simplest PAHs, DAPs have attracted significant synthetic attention, in terms of their intriguing optoelectronic properties and important graphene segments.[7] Among many efforts, the transformations through the formation of various metallacycle species **E** or **F** have been considered as most effective synthetic methods (Scheme 1d).[8] In comparison, our reaction was designed to proceed through the cleavage of three chemical bonds to form two new C–C bonds in one shot and the starting AFs **1** can be readily accessible by the condensation of aryl aldehydes with 9*H*-fluorene (Scheme 1c). In this context, the desired metal-free tandem oxidation is considered to be a highly atom-economic and straightforward method to construct DAPs.

In order to investigate the feasibility of our assumptions, we began our studies by optimizing various single electron oxidation systems for the intermolecular reaction of a readily accessible benzylidene fluorene **1a** with *o*-xylene **2a** as an aromatic nucleophile (see Table 1). The previously employed oxidation conditions, such as the combination of DDQ with Cu(OTf)$_2$ and TBPB/CuCl with trifluoroacetic acid (TFA, 5 equiv),[5b,c] did not afford the desired product **3aa** (Table 1, entries 1 and 2). In addition, the DDQ and TFA (10 equiv) combination system in dichloroethane solvent at 80 °C afforded the desired product **3aa** in low yield with significant decomposition of **1a** (Table 1, entry 3). It was noted that, upon treating **1a** with the aforementioned oxidation condition in the absence of **2a**, a mixture of the undesired oxidative dimerization and trimerization products of **1a** were detected by high-resolution mass spectrometry. Fortunately, the best result was obtained with DDQ, using TFA as the solvent at room temperature; thus, the corresponding product **3aa** was formed in a high yield of 95% (Table 1, entry 4). Among the other acids that were examined as a solvent with DDQ, the relatively weak acid (acetic acid, AcOH) was totally inactive and the strong acid (methanesulfonic acid, MsOH), afforded the formal intermolecular Friedel–Crafts reaction product **3aa′** as a major product without forming the desired **3aa** (Table 1, entries 5 and 6). Other oxidants such as *p*-chloranil and *o*-chloranil, combined with TFA, led to no reaction or a low yield of **3aa** (Table 1, entries 7 and 8). The present tandem oxidation did not occur if TFA or DDQ was used solely (Table 1, entries 9 and 10). Note that other byproducts arising from the aforementioned side reactions were not observed in the reaction mixture, indicating the indispensable role of the DDQ/TFA system for the selective implementation of the present tandem oxidation.

Table 1. Optimization of Oxidation Conditions for the Formation of 3aa



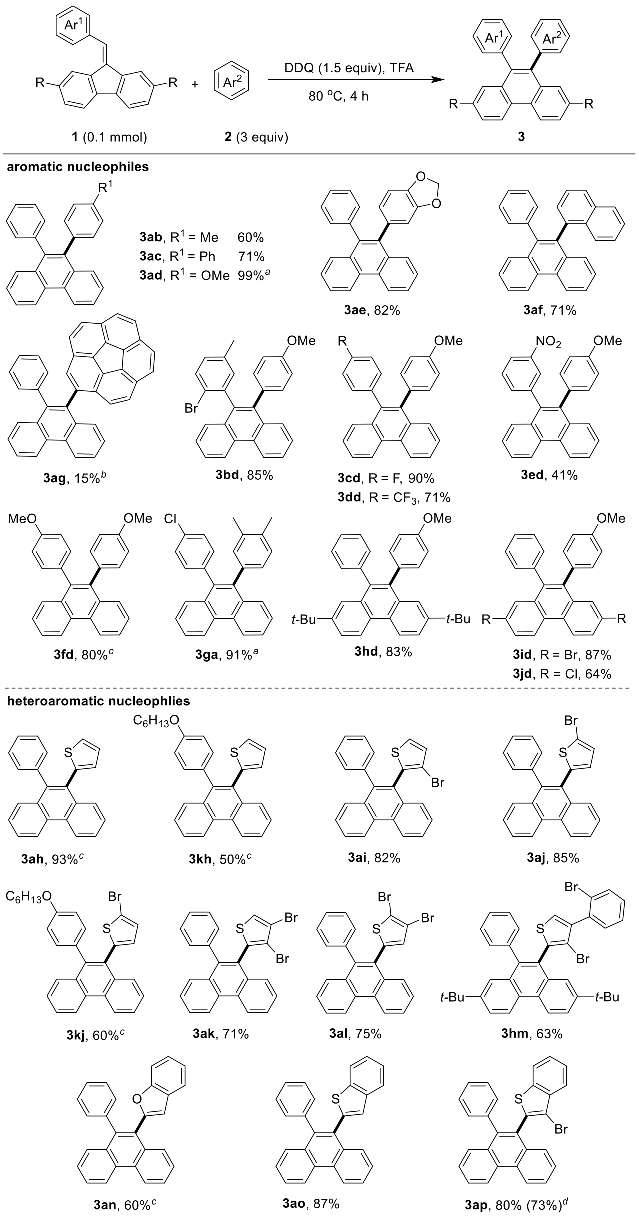
				Yield^a (%)	
entry	oxidant	acid (equiv)	solvent (0.17 M)	3aa	1a
1^b	DDQ	Cu(OTf)$_2$ (0.3)	DCM	0	86
2^c	TBPB/CuCl	TFA (5)	*o*-xylene	<5	0
3^d	DDQ	TFA (10)	DCE	27	22
4	DDQ	–	TFA	(95)	0
5	DDQ	–	AcOH	0	99
6^e	DDQ	–	MsOH	0	0
7	*p*-chloranil	–	TFA	0	96
8	*o*-chloranil	–	TFA	30	21
9	–	–	TFA	0	75
10	DDQ	–	DCE	0	99

^{a}Yields were determined by ^{1}H NMR spectroscopy, using CH$_2$Br$_2$ as an internal standard. Isolated yield was given in parentheses. ^{b}2.5 equiv of DDQ was used at 40 °C. ^{c}2 equiv of TBPB and 20 mol % of CuCl were used in *o*-xylene solvent at 80 °C. ^{d}The reaction temperature was 80 °C. ^{e}**3aa′** was obtained in 50% yield.

Under the DDQ/TFA oxidation conditions, we investigated the influence of various arylidene fluorenes, and aromatic nucleophiles on the selectivity and efficiency of the present tandem oxidation (Scheme 2). The reactions of **1a** with relatively weak nucleophiles, such as toluene and biphenyl, afforded the corresponding products **3ab** and **3ac** in goods yields with an exclusive *para*-selectivity at elevated temperature (80 °C). The electron-rich anisole and benzo[*d*][1,3]dioxole were tested to be reactive nucleophiles, thus transforming **1a** into the corresponding DAPs **3ad** and **3ae** in high yields. Polycyclic arenes such as naphthalene and corannulene also can be used as nucleophiles, giving rise to the tandem oxidation with **1a** to produce the corresponding DAPs **3af** and **3ag**, albeit a low yield of the latter, because of the low nucleophilicity of corannulene. Negligible electronic effect of various electron-withdrawing and electron-donating substituents on the arylidene moiety of **1b**–**1g** was observed for the reaction with anisole and *o*-xylene, affording the corresponding DAPs **3bd**–**3ga** in good to high yields. Similarly, the electron-donating *t*-butyl and the electron-withdrawing Br or Cl groups on the fluorene moiety did not show a significant electronic effect on the reaction efficiency, giving the corresponding DAPs **3hd**–**3jd** in good yields.

Thiophene is one of the most widely employed arene components in both small molecules and polymeric organic electronic materials.[9] The present tandem oxidation showed high compatibility with thiophene nucleophiles. The reaction of **1a** or **1k** with the parent thiophene afforded the corresponding thienyl-substituted DAPs **3ah** and **3kh** in 93% and 50% yields, respectively, under the DDQ/TFA/DCE oxidation conditions. Interestingly, the monobromo- and dibromo-substituted thiophenes also can be used as reactive nucleophiles, transforming **1a**, **1k**, and **1h** into the corresponding DAPs **3ai**–**3hm** in good to high yields with an exclusive site selectivity of thiophenes. These bromo-substituted DAPs could be further functionalized by various coupling reactions, whereas they are not easy to achieve by the conventional transition-metal-mediated synthetic methods.[8] Similarly, benzofuran and benzothiophene were also competent nucleophiles, affording the corresponding DAPs **3an**–**3ap** in satisfactory yields. The reaction can be applied to the gram-scale and thus the use of 5 mmol of **1a** with 3-bromobenzothiophene produced **3ap** in 73% yield (1.71 g), emphasizing the practical synthetic application of this method.

Scheme 2. Substrate Scope of Arylidene Fluorenes and Aromatic Nucleophiles

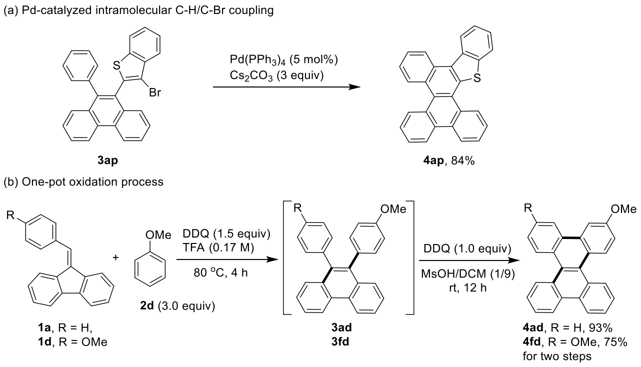


^{a}DDQ (1.5 equiv), TFA (0.17 M), rt, 4 h. ^{b}Corannulene was recovered in 75% yield. ^{c}DDQ (1.5 equiv), TFA (10 equiv), DCE (0.25 M), 80 °C, 4 h. ^{d}Yield of a 5 mmol (**1a**) scale reaction is shown in parentheses.

We briefly summarized the compatibility and limitation of the employed nucleophilic aromatics based on Mayr's database of reactivity parameters[10] in order to better understand and predict suitable nucleophiles, with respect to optimal reaction conditions. A rough nucleophilicity cutoff of aromatic nucleophiles for this reaction is in the range of $-4.36 < N < -1.01$ (where N represents the nucleophilicity parameter),[11] indicating that a broad scope of aromatic nucleophiles with weak to moderate nucleophilicity can be applicable in this reaction. For example, the reaction of **1a** with a weak nucleophilic toluene ($N = -4.36$) required a high temperature of 80 °C (DDQ/TFA solvent), whereas the reaction proceeded at room temperature (DDQ/TFA solvent) with anisole, having a moderate nucleophilicity ($N = -1.18$). Again, relatively mild conditions (DDQ/TFA/DCE solvent) were required for the reaction with the heteroaromatic nucleophile, such as thiophene, because of its relatively strong nucleophilicity ($N = -1.01$). In comparison, the very weak benzene nucleophile ($N = -6.3$) and the strong N-methylindole nucleophile ($N = 5.75$) showed a detrimental effect on the reaction outcome,[12] yielding no desired products.

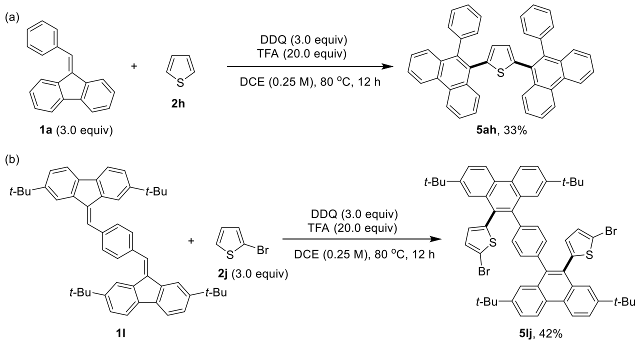
The synthetic applications for constructing π-extended PAHs have been investigated. For example, the Pd-catalyzed intramolecular C−H/C-Br coupling of the resulting product **3ap** afforded the corresponding DBC derivative **4ap**, benzo[*b*]benzo[11,12]chryseno[6,5-*d*]thiophene, in 84% yield (Scheme 3a). We also demonstrated that the one-pot oxidation process could directly affect the DBC framework. For example, after the oxidation of **1a** or **1f** with anisole under the present reaction conditions, the resulting reaction mixture was directly subjected with the DDQ/MsOH oxidation system (Scheme 3b). As a result, the intermolecular tandem oxidation and subsequent intramolecular oxidative aromatic coupling reaction[6a] occurred in one pot to give the corresponding DBCs **4ad** and **4fd** in good to high yields.

Scheme 3. Synthetic Applications toward Dibenzo[*g*,*p*]chrysene Derivatives

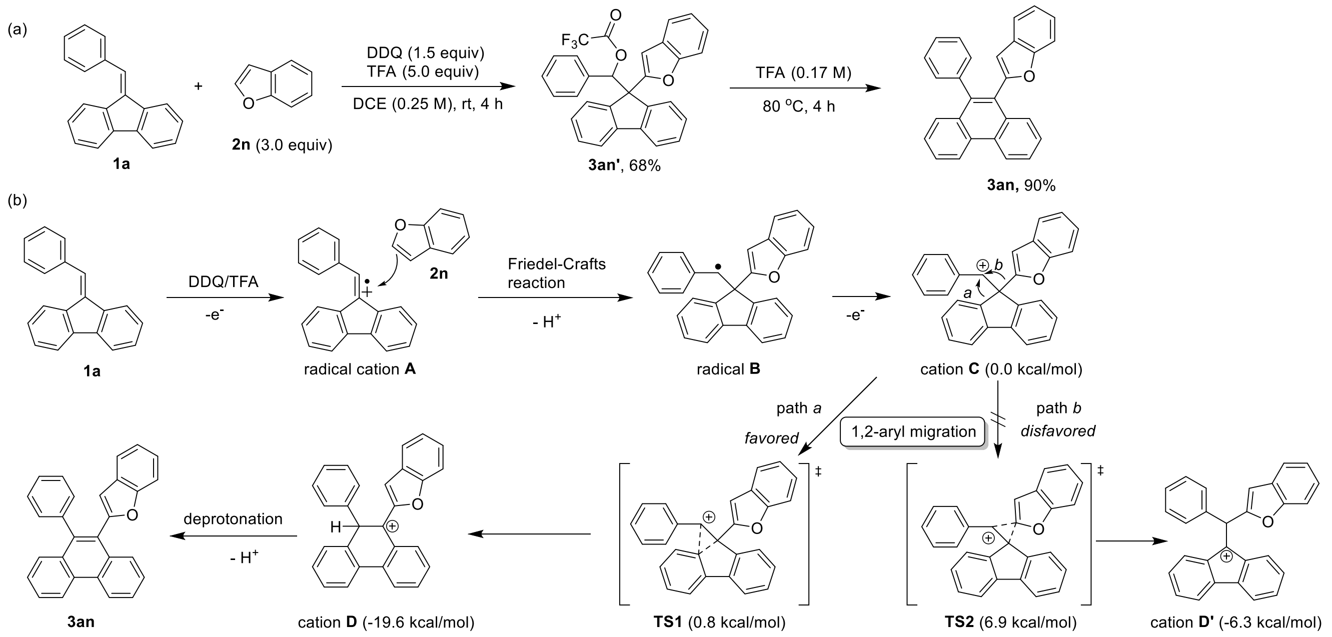


Furthermore, the phenanthrene end-capped co-oligomers could be synthesized through this 2-fold tandem oxidation. For example, the reaction of 3 equiv of **1a** with the parent thiophene **2h** under the modified tandem oxidation conditions afforded the phenanthrene end-capped thiophene co-oligomers **5ah** in 33% yield (Scheme 4a). Similarly, the 2-fold tandem oxidation of the BF-dimer **1l** with 3 equiv of 2-bromothiophene **2j** led to the corresponding co-oligomer **5lj** in 42% yield (Scheme 4b). It is interesting to stress that this 2-fold process proceeds through the cleavage of six C−H and C−C bonds to form four new C−C

Scheme 4. Two-Fold Tandem Oxidation for Phenanthrene End-Capped Co-oligomers



Scheme 5. Control Experiments and Proposed Reaction Mechanism[a]



[a] Relative Gibbs free energies of the intermediates and transition states by DFT calculation at the level of ωB97XD/6-31G(d,p) are shown in parentheses. Trifluoroacetate was used as an anion in DFT calculation. 2,2,2-Trifluoroethanol was used as solvent in DFT calculation, because of its same dielectric constant with TFA.

bonds in one shot, which should be highly attractive for the construction of π-extended complex molecules.

We then performed control experiments to elucidate the mechanism (Scheme 5a). The reaction of **1a** with benzofuran **2n** under the modified oxidation conditions, DDQ (1.5 equiv) and TFA (5.0 equiv) in DCE at room temperature, the trifluoroacetyl and benzofuran disubstituted product **3an′** was isolated in 68% yield, which was determined unambiguously by X-ray crystallography (see Figure S1 in the Supporting Information). Interestingly, upon subjecting **3an′** with TFA at 80 °C, the desired ring expansion product **3an** was formed in 90% yield. These results strongly suggested that benzofuran initially attacked preferentially at the cationic C atom on the five-membered ring and the 1,2-aryl migration-induced ring expansion proceeded under the acidic conditions through the formation of a benzylic cation **C**. The proposed reaction mechanism is outlined in Scheme 5b (see Figure S2 in the Supporting Information). A single electron oxidation occurs preferentially at the more-electron-rich alkenyl moiety of **1a** by the DDQ/TFA oxidation system to form a radical cation species **A**.[5b] Subsequently, the benzofuran nucleophile and the radical cation **A** undergoes an intermolecular Friedel−Crafts reaction, leading to the formation of a benzylic radical species **B**, which should be further oxidized to a benzylic cation **C**. Two 1,2-aryl migration paths through the migration of an aryl group of the fluorene moiety by ring expansion (path *a*) and the benzofuran group (path *b*) in the intermediate **C** can be considered. The density functional theory (DFT) calculations showed that the activation energy barriers for the transition state **TS1** through path *a* and the transition state **TS2** through path *b* are 0.8 and 6.9 kcal/mol, respectively, indicating that the 1,2-aryl migration through a ring expansion is more favorable than that through a benzofuran migration. In addition, the carbocation intermediate **D** resulting from path *a* is energetically 13.3 kcal/mol more stable than the carbocation intermediate **D′** resulting from path *b*. In addition, we did not observe any byproducts arising from the intermediate **D′** and, thus, the 1,2-aryl shift via path *b* can be excluded. Finally, the rapid deprotonation of the carbocation **D** yields the aromatized product **3an**.

In conclusion, we have developed a new metal-free and highly efficient intermolecular tandem oxidation between AFs and various unfunctionalized aromatics for constructing structurally important and useful DAPs under the DDQ/TFA oxidation conditions. The formation of a radical cation species at the alkenyl moiety of the AFs is a key feature to induce subsequent intermolecular oxidative Friedel−Crafts reaction and ring expansion tandem process, transforming readily accessible AFs and unfunctionalized arenes into the desired DAPs with excellent functional group tolerance and exclusive chemo-selectivity. Moreover, we have demonstrated that the present tandem oxidation can be applied to one-pot and 2-fold processes to access π-extended PAHs and co-oligomers. Further extension of the present synthetic protocol to construct medium-sized ring-fused PAHs are in progress, which may open a new and alternative avenue to access various planar and curved PAHs.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03283.

Experimental procedures and characterization of related compounds (PDF)

Accession Codes

CCDC 2027514 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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