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Annulation

Aerobic Dimerization of Enediyne Compounds: Construction of Naphthalene Frameworks

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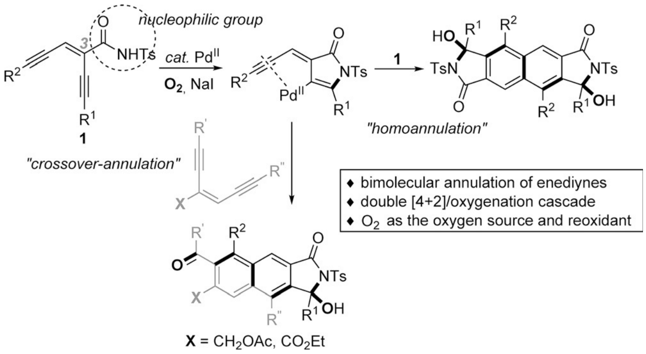
Abstract: The first bimolecular oxygenative annulation of enediyne compounds leading to naphthalene frameworks has been developed by using $Pd(OAc)_2$ as the catalyst in the presence of NaI under O_2 (1 atm). This reaction provided efficient access to a class of symmetric core-annulated naphthalenes by the homoannulation of enediyne–imides. Intriguingly, the crossover annulation of enediyne–imides and other functionalized enediynes could also be achieved by the same catalytic system, resulting in the formation of several unsymmetrical naphthalene derivatives. Preliminary mechanistic investigation using ^{18}O isotopic labelling and radical scavengers indicated that radical oxygen incorporation cascades might be involved in this conversion.

Selective synthesis of polysubstituted polycyclic aromatic hydrocarbons (PAHs) is of great interest because of their increasing application in materials science and supramolecular chemistry.[1] During the past decade, significant progress has been achieved in PAH synthesis by transition-metal-catalyzed reactions, which predominately utilize benzenoid substrates for the synthesis of naphthalene frameworks.[2] For instance, various transition-metal-catalyzed cyclization reactions, including the [4+2] benzannulation of a given aryl substrate with alkynes,[3b–l] are among the most efficient tools for the construction of condensed aromatics.[3] Meanwhile, using a late-stage diversification strategy, several promising protocols have recently been developed based upon a transition-metal-catalyzed C–H functionalization, which provides an expedient access to diversely substituted PAHs.[4] Despite these impressive advances, given recent rising demands for core-substituted and core-annulated naphthalene derivatives,[5] novel synthetic methods, particularly those enabling the regioisomer-free formation of functionalized naphthalene compounds, remain highly desirable.[6]

Fuelled by the sustained progress in the Bergman reaction[7] and the Schreiner–Pascal cyclization,[8] the cycloaromatization of benzenoid enediynes has emerged as a promising approach for the generation of aromatic products in recent years.[9,10] As a complementary alternate to this reductive cycloaromatization of enediynes, we have recently reported a formal Pd/Cu-catalyzed aerobic [4+2] cross-benzannulation of readily accessible enediyne–imides **1** and internal alkynes using a directing group strategy to overcome the innate cycloisomerization tendency of enediyne subunits.[11,12] In the light of this result, herein we present a novel dimerization approach for the construction of naphthalene frameworks through a nucleophilic-directing-group-triggered, Pd^{II}-catalyzed, intermolecular aerobic oxidative annulation of 3-functionalized enediynes by using molecular O_2 (1 atm) as the oxygen source and reoxidant in the presence of NaI (Scheme 1).[13]



Scheme 1. Aerobic annulation cascades of enediyne compounds.

The initial assays were triggered by the finding of trace amounts of naphthalene derivative **2a** as mixtures of a pair of diastereoisomers (d.r. = 1:1) when subjecting enediyne–imide **1a** to $Pd(OAc)_2$ (10 mol%) in DMF at 25 °C in air (Table 1). While elevating the reaction temperature to 60 °C gave **2a** in 23% yield under O_2 (1 atm), the addition of $CuBr_2$ sharply improved the yield of **2a** to 52% (entries 1 and 2). Further exploration of the additives revealed that alkali halide salts could also promote this Pd^{II}-catalyzed aerobic transformation[14] of **1a** to **2a** (entries 3–5). An extra addition of stoichiometric amounts of 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO; 2 equiv) decreased the reaction rate but had little effect on the yield (entry 6), suggesting that a radical reaction might be involved. In the presence of NaI, both $PdCl_2$ and $Pd(acac)_2$ showed the catalytic activity but led to a lower yield (entries 7 and 8). Switching the solvent to DMSO or DMA reduced the yield of **2a** (entries 9 and 10). Furthermore, it was found that molecular sieves (3 Å) promoted the formation of **2a** (entry 11; 81% yield). In contrast, only a trace amount of **2a** was observed

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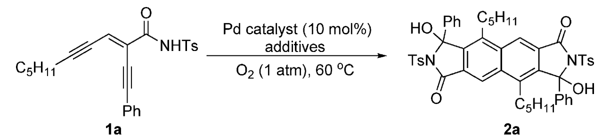
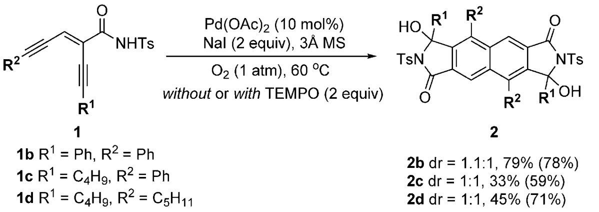
Table 1. Optimization of reaction conditions.[a]



Entry	Catalyst	Additives	Solvent	Yield [%][b]
1	$Pd(OAc)_2$	–	DMF	23
2[c]	$PdCl_2$	$CuBr_2$	DMF	52
3	$Pd(OAc)_2$	NaBr	DMF	58
4	$Pd(OAc)_2$	LiCl	DMF	49
5	$Pd(OAc)_2$	NaI	DMF	73
6[d]	$Pd(OAc)_2$	NaI/TEMPO	DMF	71
7	$PdCl_2$	NaI	DMF	56
8	$Pd(acac)_2$	NaI	DMF	55
9	$Pd(OAc)_2$	NaI	DMSO	27
10	$Pd(OAc)_2$	NaI	DMA	46
11[e]	$Pd(OAc)_2$	NaI	DMF	81
12[f]	$Pd(OAc)_2$	NaI	DMF	<5
13	–	NaI	DMF	–

[a] Unless otherwise noted, the reaction was carried out at 60 °C using **1a** (0.1 mmol), catalyst (10 mol%), and additives (2 equiv) in anhydrous solvent (1.0 mL) under O_2 (1 atm) for 18 h. [b] Isolated yield. [c] $CuBr_2$ (0.2 equiv) used. [d] For 24 h. [e] Molecular sieves (3 Å, 100 mg) were used. [f] Under N_2.

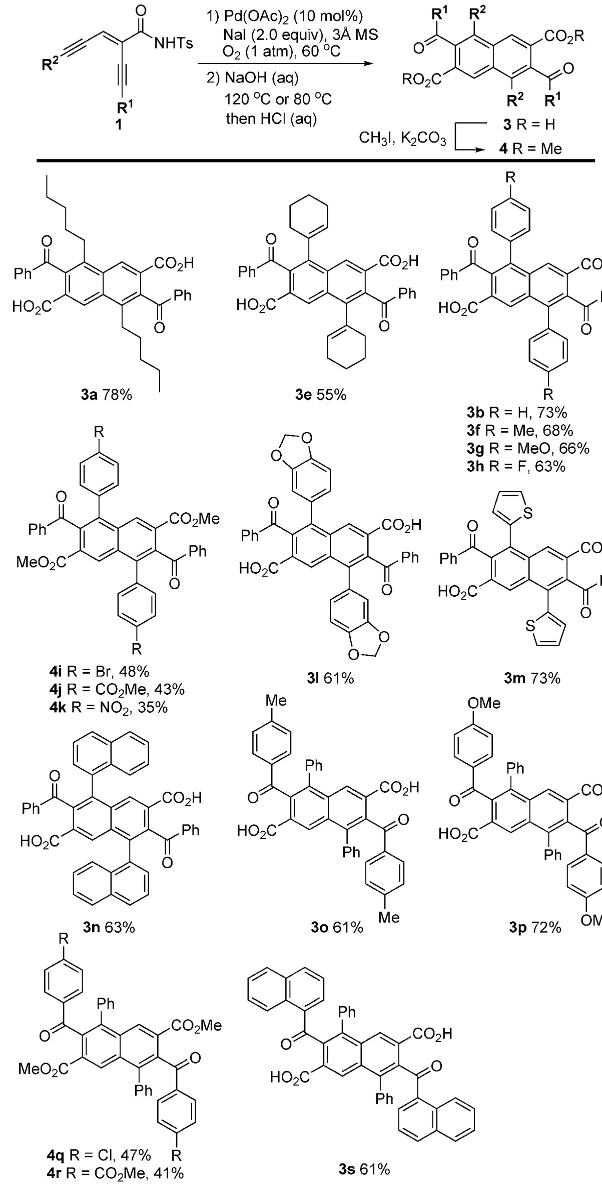


Scheme 2. Synthesis of naphthalene derivatives **2**. Yields in parenthesis were obtained in the presence of TEMPO (2 equiv).

under N_2, and no desired product was detected in the absence of $Pd(OAc)_2$ (entries 12 and 13), indicating that both palladium catalysts and O_2 are required for this conversion.

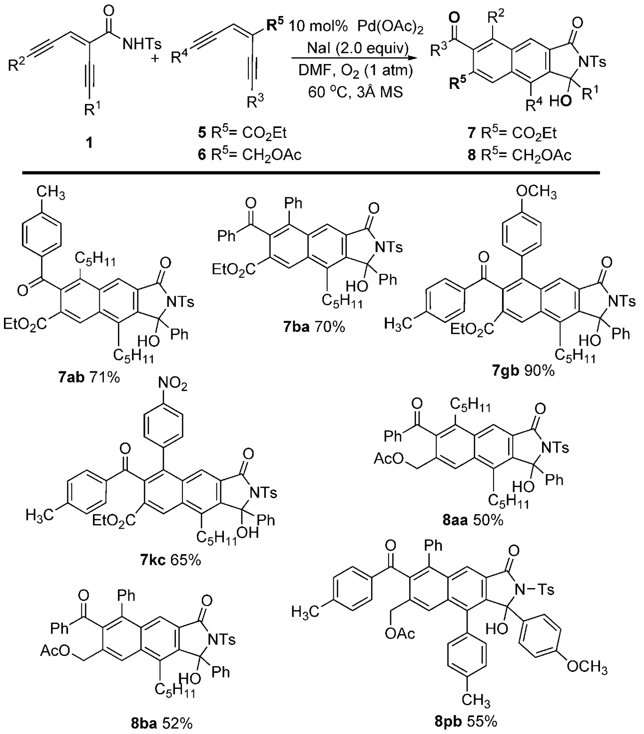
A brief study on the substrate scope was firstly screened (Scheme 2). The reaction of diphenyl-substituted enediyne **1b** proceeded smoothly to give **2b** in 79% yield.[15] Introducing alkyl groups as the R^2 substituent on **1** delivered the desired products **2c** and **2d** in lower yields. Compared with the aryl-substituted counterpart **1b**, intriguingly, **1c** and **1d** underwent this reaction more efficiently in the presence of TEMPO (2 equiv), resulting in an approximate 30% increase in isolated yields of the products. This suggests that TEMPO probably participated in these transformations and facilitated the incorporation of oxygen into **1c** and **1d**.

Next, a two-step, one-pot protocol was established to furnish dicarboxylic acids **3**, which are difficult to be synthesized in a regioisomer-free fashion by existing methods (Scheme 3). Thus acid **3a** was obtained in 78% yield from **1a** after hydrolysis under basic conditions. The variation of the R^2 substituent on **1** was then examined. An alkenyl group was employed to produce **3e** in 55% yield. Various 4-substituted benzene rings no matter containing an electron-donating (-Me or -OMe), -withdrawing ($-NO_2$ or $-CO_2Me$), or a halogen group (F or Br) were well tolerated to yield the targeted products. Due to the reason of product solubility, esters **4i**–**4k** were isolated as the products instead of the corresponding diacids upon treatment with CH_3I. Other aromatic rings, including benzo[*d*][1,3]dioxol-5-yl (**3l**), thienyl (**3m**), and naphthyl (**3n**), could also be used in this reaction successfully. On the other hand, variation of the R^1 substituent showed that a set of electron-rich and -poor phenyl groups and a naphthyl unit were suitable for this transformation to give the desired products (**3o**, **3p**, **4q**, **4r**, and **3s**).

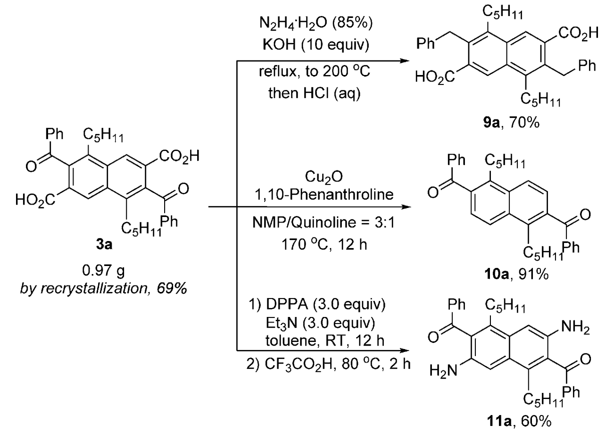


Scheme 3. Synthesis of **3** and **4**. Reaction conditions: 1) **1** (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), NaI (60 mg, 0.4 mmol), and 3 Å MS (100 mg) in DMF (2 mL) under O_2 (1 atm) at 60 °C for 18 h; 2) NaOH (aq), and DMSO at 120 °C or 80 °C (for **3l** and **4k**, respectively). Yields are of the isolated products.

Gratifying, the aerobic heterodimerizations of **1** with other functionalized enediynes **5** and **6** could also be achieved



Scheme 4. Synthesis of products **7** and **8**. Reaction conditions: **1** (0.1 mmol), **5** or **6** (0.3 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), NaI (30 mg, 0.2 mmol), and 3 Å MS (100 mg) in DMF (1 mL) under O_2 (1 atm) at 60 °C for 5 h. Yields are of the isolated products.

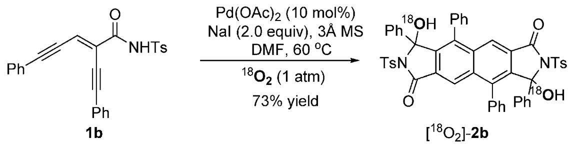


Scheme 5. Transformation of naphthalenedicarboxylic acid **3a**.

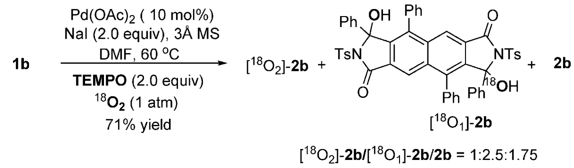
under the standard reaction conditions, thus significantly expanding the synthetic application of the current protocol (Scheme 4). Both aryl- and alkyl-substituted enediyne–imides **1** underwent the aerobic crossover annulations with a set of esters **5** smoothly, giving access to ketone esters **7** in good yields. Remarkably, fully differentiated hexasubstituted naphthalene cores could be assembled selectively, for example, the formation of **7gb** and **7kc** in 65% and 90% isolated yields, respectively. Moreover, acetate **6** was also tolerated in annulations with **1** to deliver the corresponding products **8** in moderate yields.[16]

The cyclic dimerization protocol could be easily conducted on a multigram scale, for example, to give acid **3a** in 69% yield (see the Supporting Information). Further investigation demonstrated that **3a** represented a flexible platform for further manipulations (Scheme 5). While the Wolff–Kishner reduction of **3a** led to the formation of diarylmethane **9a**, the copper-catalyzed protodecarboxylation of **3a** delivered diarylketone **10a** in high yield.[17] Furthermore, the conversion of carboxylic moieties of **3a** to amine groups by the Curtius rearrangement and subsequent hydrolysis afforded **11a** in 60% overall yield.

The reaction of **1b** under standard conditions using $^{18}O_2$ (1atm) predominately afforded [$^{18}O_2$]-**2b**, which incorporated two ^{18}O atoms into the hydroxyl groups as detected by HRMS [Eq. (1)]. When the same reaction was conducted in the presence of TEMPO (2 equiv), mixtures of [$^{18}O_2$]-**2b**, [$^{18}O_1$]-**2b**, and **2b** were obtained in 71% combined yield in a ratio of about 1:2.5:1.75 as detected by HRMS analysis [Eq. (2)]. These results clearly indicated that the oxygen incorporation process occurred via radical intermediates, which could be trapped by molecular O_2 or TEMPO to form the products. Nevertheless, attempts to capture the related TEMPO adduct intermediates failed, presumably because these adducts were too labile to decompose into the products under the current reaction conditions through in situ cleavage of the N–O bond of TEMPO adducts. In this case, an incomplete incorporation of ^{18}O label occurred. The aforementioned observations of the increased yield of **2c** and **2d** in the presence of TEMPO could be attributed to the positive effects arising from the participation of TEMPO.

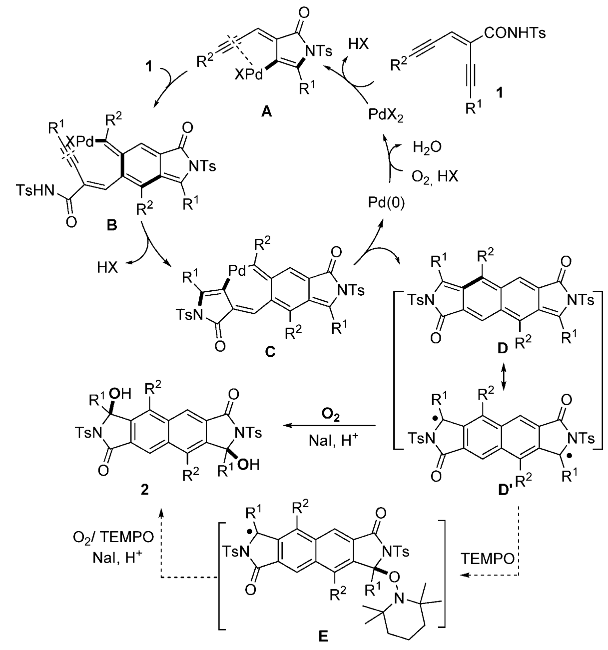


(1)



(2)

A tentative mechanism for the formation of homodimers **2** is presented in Scheme 6. Initial intramolecular cyclization of enediyne **1** by a 5-*endo*-dig *anti*-aminopalladation would give vinylpalladium species **A**,[18] which undergoes a sequential twofold carbopalladation cascade selectively with one alkyne moiety of another molecule of **1**, providing access to intermediate **B.**[19] Subsequent 5-*endo* aminopalladation of **B** to **C** followed by a reductive elimination would release putative polyene **D** and a Pd^0 species, which could be regenerated to the active Pd^{II} catalyst by HX and O_2.[20] Delocalized Kekulé-type diradical **D**′[21] could be trapped by O_2 and finally **2** is furnished upon treatment with NaI.[22] In the presence of TEMPO,



Scheme 6. Proposed reaction pathway to **2**.

an alternative addition of TEMPO onto the conjugated polyene **D** leading to intermediate radical **E** might be involved, wherein the later radical **E** could be further captured by O_2 or TEMPO and yields **2** in situ.[23]

In summary, we have presented a flexible aerobic enediyne cyclic dimerization strategy for the synthesis of polysubstituted naphthalene frameworks through Pd^{II}-catalyzed intermolecular aerobic oxidative annulations of enediyne compounds using O_2 (1 atm) as the oxygen source and reoxidant in the presence of NaI. Preliminary studies revealed that the heat-induced aromatization and potential TEMPO-triggered aromatization could be responsible for the oxygen incorporation procedure during the formation of homodimerization products. Further investigations focused on elucidating the mechanistic details as well as exploiting novel intermolecular reactions of enediynes are underway.

Acknowledgements

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Keywords: cycloaddition · dimerization · enynes · palladium · polycycles

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[15] CCDC 1051503 (*trans*-**2b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[16] Only trace amounts of the corresponding products arising from the homodimerization of enediyne–imides **1** were observed using 3 equivalents of enediynes **5** or **6**. Reducing the loading of **5** or **6** to 1.5 equivalents would prompt the homodimerization of **1**, resulting in a roughly 15% decrease in isolated yields of the products **7** and **8**.

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