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Pd-catalyzed dehydrogenative annulation approach for the efficient synthesis of phenanthridinones†

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A novel Pd-catalyzed intermolecular dehydrogenative annulation of aryl iodides and aryl carbamic chlorides for the efficient synthesis of phenanthridinone derivatives was developed. Simple aryl iodides and carbamic chlorides readily made from various anilines, a broad substrate scope with hetero/polycycles, as well as high-value products, make this direct dehydrogenative annulation approach very practical and attractive.
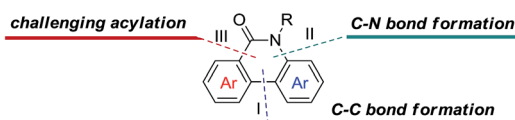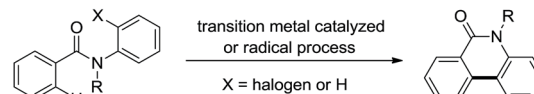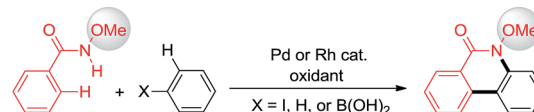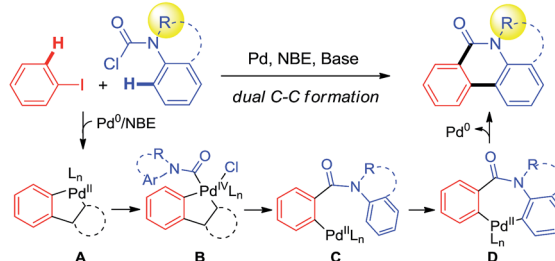
Introduction

Phenanthridinones are ubiquitous fused heterocyclic motifs found in many natural alkaloids and pharmaceutically active compounds, exhibiting broad biological activities such as antitumor, antivirus, and DNA topoisomerase I inhibition.[1] The rising use of these biologically significant fused phenanthridinones has stimulated considerable interest in developing their synthetic methods with enhanced generality, scope, and cost effectiveness. Accordingly, many synthetic approaches, including annulation of prefunctionalized substrates to construct phenanthridinones and their derivatives, were developed in the past decades.[2] Despite their significance, most of reported methods suffer from the prefunctionalized substrates low efficiency or limited substrate scope. Therefore, direct strategies for the efficient synthesis of diverse phenanthridinones are still highly demanded.

Transition-metal-catalyzed dehydrogenative annulation of simple substrates has proven to be a versatile and powerful synthetic strategy to construct polycyclic and heteroaromatic compounds.[3] The retrosynthetic analysis of phenanthridinones through a dehydrogenative strategy could be orientated to typical C–C bond formation (I), amide directed C–N bond formation (II), or acylation (III) (Scheme 1a). Using a one chemical bond formation strategy, the intramolecular dehydrogenative cyclization of aryl amides *via* path I has been significantly developed by the groups of Åkermark,[4a] Fagnou,[4b] Dong,[4c] Cheng,[4d] and Curran[4e] (Scheme 1b).

In order to disclose new approaches from more simple substrates, a strategy using two chemical bond formation is desired. Recently, Wang[5] and Cheng[6] independently developed elegant Pd- or Rh-catalyzed intermolecular dehydrogenative cyclization *via* C–C and C–N bond formation (pathways I and II) to prepare *N*-methoxy phenanthridinones (Scheme 1c). However, despite the significance, the requirement of stoichiometric oxidant and the CONHOMe directing group limit

Scheme 1 Dehydrogenative annulation strategies for phenanthridinone construction.

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the substrate scope and their application in the construction of hetero and polycycles. Alternatively, a straightforward approach through two C–C bond formation (pathways I and III) (Scheme 1a) enables the use of various functional groups including some heterocyclic partners from corresponding readily available aniline precursors (Scheme 1d). However, to the best of our knowledge, this strategy is still unknown and poses a challenge due to the adjacent dual C–C bond construction via C–H bond cleavage.[7]

Recently, Pd/norbornene (NBE) chemistry has been demonstrated to be a significant protocol that allows activation of both the ipso and ortho-positions of arenes.[8,9] In continuation of our interest in dehydrogenative annulation for the construction of heterocycles,[10] we envisioned that if a proper carbonyl reagent could be employed to form Pd[IV] intermediate **B** through the palladacycle **A** species generated in situ from aryl iodides in the presence of NBE, acylation at the ortho-position would be realized and produce the aryl-Pd intermediate **C**. Subsequently, if species **C** could undergo the CMD[11] process, followed by reductive elimination to realize arylation,[12] the desired phenanthridinone derivatives would be constructed (Scheme 1d). Very recently, Dong,[13a] Gu,[13b] and Liang[13c] independently reported unprecedented ortho C–H acylation of aryl iodides through Pd/NBE chemistry. These results encouraged us to test the above dehydrogenative design. Nevertheless, three challenges have to be solved: (1) the carbonyl reagent not only needs to provide the carbonyl group but also has to be a stronger oxidant than aryl halides, to avoid homo-Catellani coupling,[14] for oxidizing **A**. (2) The subsequent dehydrogenative annulation that implicates the intermediacy of seven-membered palladacycle **D** should be favoured over other quenched processes. (3) Multiple steps including acylation and annulation have to take place successively under mild conditions. Herein, we report the discovery of a novel Pd-catalyzed dehydrogenative annulation of aryl iodides and aryl carbamic chlorides for the efficient synthesis of phenanthridinones (Scheme 1d).

Results and discussion

Initially, we endeavoured to realize the Pd-catalyzed dehydrogenative annulation reaction using iodobenzenes and anilines with norbornene under CO, however, only the ipso position of the iodobenzenes was carbonylated, providing liner amides without cyclization. We hypothesized that properly pre-functionalized carbonyl anilines may inhibit the carbonylation at the ipso position in order to preclude the by-products. As we expected, when 1-iodo-2-methylbenzene (**1a**) was reacted with methyl(phenyl)carbamic chloride (**2a**), the intermolecular annulation performed well affording the desired phenanthridinone **3a** (Table S1, see ESI†). The desired product, **3a**, could be obtained in up to 98% yield when using Pd(OAc)$_2$/PPh$_3$ as the metal/ligand combination, NBE, and Cs$_2$CO$_3$ as the base in DCE at 95 °C (**3a**, Table 1). A series of control experiments indicated that the palladium, phosphine ligand, NBE, and base were all essential for this transformation (entries 2–5, Table S1, see ESI†).

**Table 1** Scope of aryl carbamic chlorides with different substituents[a]
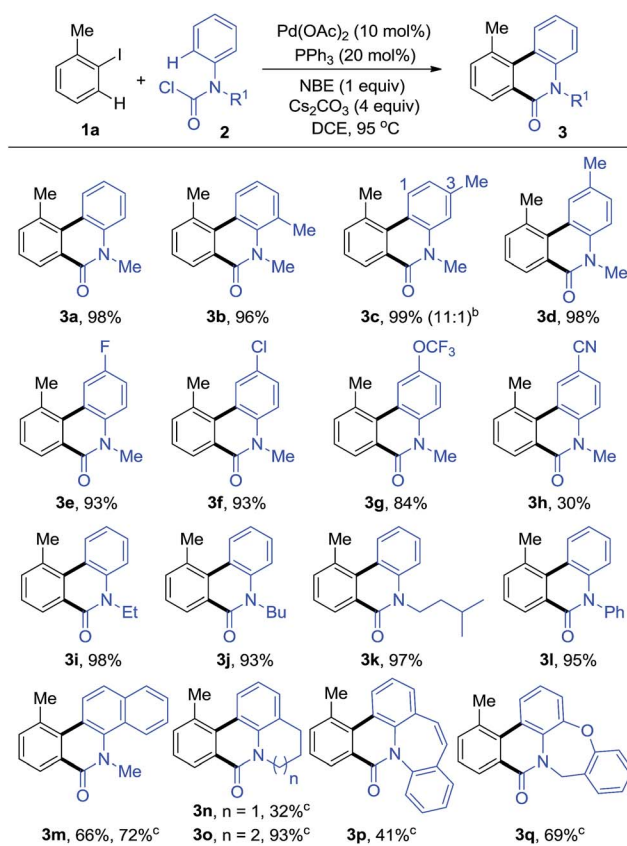
^{a} Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Pd(OAc)$_2$ (0.02 mmol), PPh$_3$ (0.04 mmol), NBE (0.2 mmol), and Cs$_2$CO$_3$ (0.8 mmol) in DCE (2 mL) at 95 °C for 6 h. ^{b} Regioselectivity ratio (the major isomer is substituted at the 3-position as drawn). ^{c} The reaction was conducted in toluene.

With the optimized reaction conditions in hand, we next explored the scope of aryl carbamic chlorides **2** (Table 1). o-, m-, p-Methyl substituents on the phenyl ring of **2** were well tolerated and the desired phenanthridinones **3b–d** were isolated in excellent yields. Among them, **3c** was synthesized with good regioselectivity. A series of **2**, bearing electron-donating groups or weak electron-withdrawing groups such as F and Cl, and OCF$_3$, were tested and showed excellent performance in this reaction, giving the corresponding products in high yields (**3d–g**). It is worthy to note that N-alkyl and aryl groups were compatible in this transformation with almost equivalent transformation into corresponding products (**3i–l**). Furthermore, methyl(naphthalen-1-yl)carbamic chloride (**2m**) and polycyclic carbamic chlorides (**2n–q**) were smoothly converted into polycyclic phenanthridinones (**3m–q**) in moderate to good yields, which are the common core structural motifs in some natural products and bioactive compounds. For these substrates, the reaction proceeded better in toluene than in DCE.

In order to explore the effect of substituents on iodobenzenes, a variety of aromatic and heteroaromatic iodides

Table 2 Substrate scope with different aryl iodides[a]
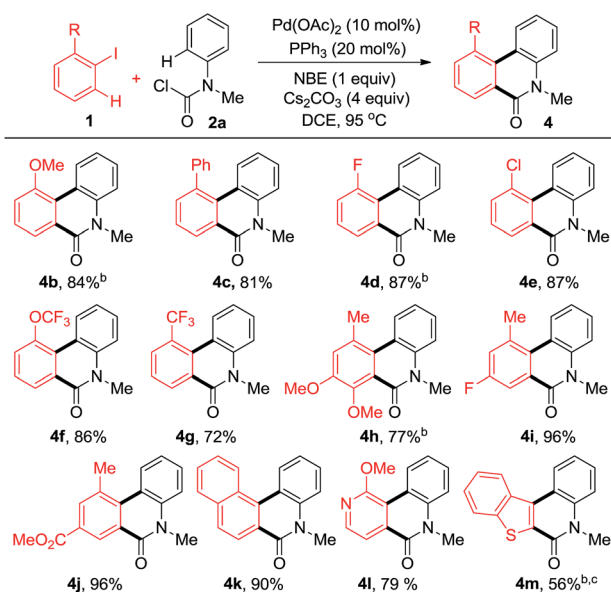
a Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), Pd(OAc)$_2$ (0.02 mmol), PPh$_3$ (0.04 mmol), NBE (0.2 mmol), and Cs$_2$CO$_3$ (0.8 mmol) in DCE (2 mL) at 95 °C for 6 h. b The reaction was conducted in toluene. c The reaction was conducted at 110 °C.

were employed (Table 2). Different kinds of electron-rich or electron-deficient aryl iodides were compatible under these reaction conditions. Multiple substituted aryl iodides with versatile groups reacted smoothly to give the corresponding products in moderate to good yields (**4h–j**). Notably, even poly and heterocyclic fused phenanthridinones (**4k–m**) could be obtained in good yields.

Scheme 2 Other substrates and isotope-labeling experiment.

In addition, other kinds of aryl carbamic chlorides were also employed in the annulation reaction (Scheme 2). Although the N–H carbamic chloride did not work, *N*-PMB and *N*-benzyl substituted carbamic chlorides (**2r–s**) could smoothly undergo the annulation to afford the phenanthridinones **3r–s** in excellent yields (eqn (1)). Furthermore, the removal of the PMB group proceeded under acidic conditions to give N–H phenanthridinone **5** in 91% yield. When allyl(phenyl)carbamic chloride (**2t**) was employed, **6a** and **6b**, instead of the expected *N*-allyl phenanthridinone, were obtained in 80% and 15% yields, respectively, which actually proceeded through acylation followed by a Heck-reaction (eqn (2)). When vinyl(phenyl)carbamic chloride (**2u**) took part in the reaction, to our surprise, two spiro-isoindolines **7a** and **7b** were formed (eqn (3)). Simple iodobenzene without an *ortho* substituent gave an unseparated mixture containing mono- and di-acylation annulation products, and unknown byproducts.

To gain insight into the mechanism, the intermolecular KIE for the annulation reaction was determined to be $k_H/k_D = 1.3$, indicating that the C–H bond cleavage should not be involved in the rate-determining step of the catalytic cycle (eqn (4)). Moreover, a linear relationship between $\log(K_R/K_H)$ and substitute constant σ is established for substituted methyl(phenyl)carbamic chloride (R = *p*-Me, *p*-H, *p*-F, *p*-Cl, *p*-OCF$_3$, and *p*-CN) (Fig. 1).[15] The resulting Hammett parameter ρ is −0.46, suggesting the reaction is substituent-sensitive and the influence of the electronic effects correspond to the oxidative addition step. Electron withdrawing substituents can decrease the negative charge in carbamic chloride to attenuate its coordination ability and thus destabilize the transition state of oxidant addition.

Based on our preliminary mechanistic studies, and assuming a 1 : 1 stoichiometry between all reaction components in the catalyst turnover to simplify the discussion, we conducted a density functional theory (DFT) calculation investigation into the direct dehydrogenative annulation of **1a** and **2a** to better understand the mechanism of this transformation (Fig. 2).[16,17] The phenyl groups in the ligand are replaced by methyl groups to save computational time but without sacrificing credibility. Initially, the oxidative addition of **1a** with Pd^0 could occur on the bisphosphine or monophosphine complex.[18] The calculations

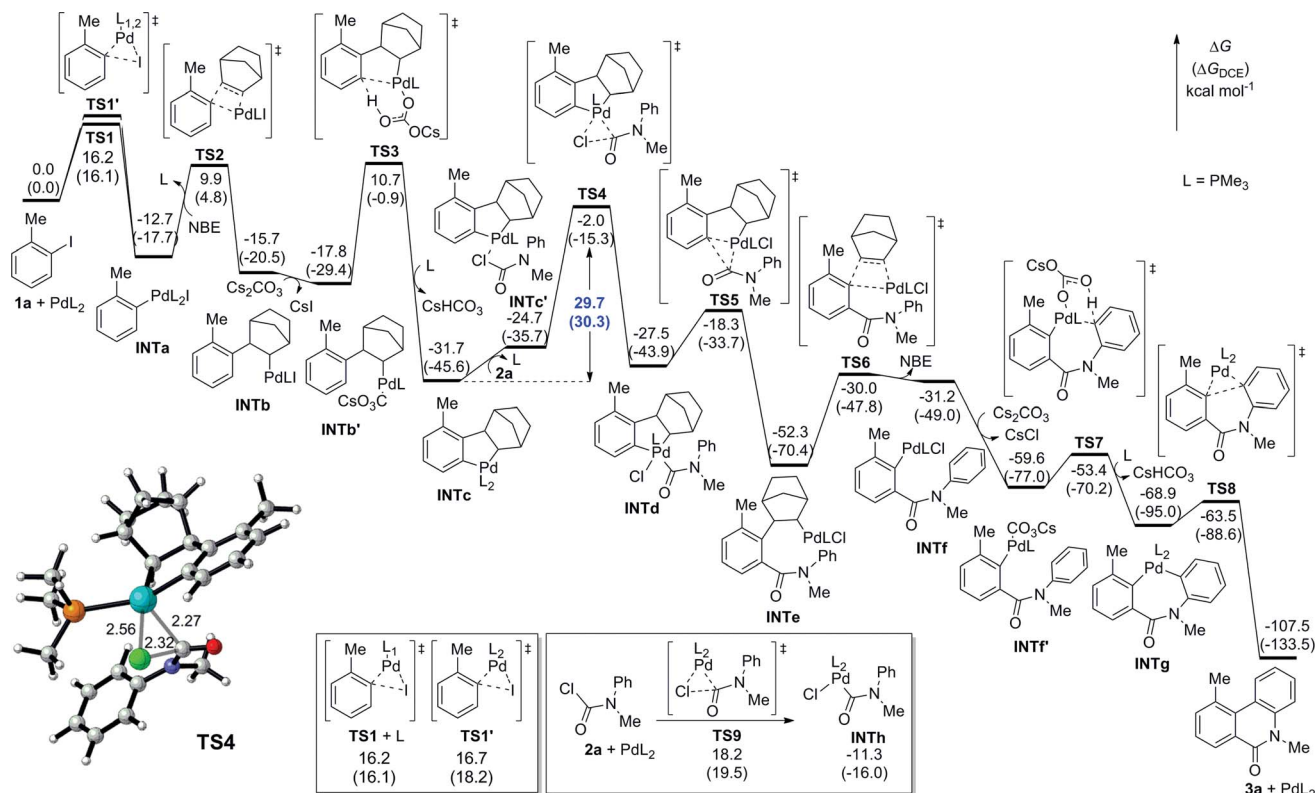**Fig. 1** Hammett plot of the annulation of **2**.

Fig. 2 DFT-computed energy profiles for Pd-catalyzed dehydrogenative acylation and annulation of **1a** and **2a**.

show that the oxidative addition on the monophosphine complex *via* transition state **TS1** is slightly favoured over that on the bisphosphine complex *via* **TS1′**, indicating that the monophosphine complex is the dominant active species, while the bisphosphine complex is the minor one (see ESI† for details). However, both pathways are facile, requiring an activation free energy of only 16.2 and 16.7 kcal mol⁻¹ to form Pd^II species **INTa** exergonicly. The next step, corresponding to the insertion of NBE, is reversible to afford **INTb**. After base exchange, the formed **INTb′** undergoes a CMD process to provide the stable intermediate palladacycle **INTc** irreversibly. Then, oxidative addition takes place through transition state **TS4** with an activation free energy of 29.7 kcal mol⁻¹ to deliver Pd^IV intermediate **INTd**. The following reductive elimination of Pd^IV is facile and exergonic. After acylation, β-C elimination of NBE occurs endergonicly. The subsequent CMD step readily proceeds to furnish cyclic intermediate **INTg**. Finally, the reductive elimination of **INTg** is also facile to give the final phenanthridinone **3a**, whilst regenerating the Pd⁰ catalyst. Reviewing the whole energy profile, we find that the direct oxidative addition of the *in situ* formed palladacycle with aryl carbamic chloride is the rate-determining step, in good agreement with the experimental observation of the Hammett plot.

Conclusions

In conclusion, we have demonstrated the first Pd-catalyzed intermolecular direct dehydrogenative annulation of aryl

iodides and aryl carbamic chlorides through dual C–H bond activation for the efficient synthesis of phenanthridinone derivatives. This protocol is easy to handle with simple aryl iodide and aryl carbamic chloride substrates readily prepared from various anilines. The use of various functional groups, including some heterocyclic partners, makes this approach very attractive for the construction of high-value and biologically significant phenanthridinone heterocycles. Preliminary experiments and DFT calculations suggest that the *in situ* formed palladacycle **INTc** could undergo oxidative addition of aryl carbamic chloride to generate a Pd^IV intermediate in the rate-determining step. Efforts toward expanding the reaction scope of other fused heterocycles are underway.

Acknowledgements

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