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A denitrogenative palladium-catalyzed cascade for regioselective synthesis of fluorenes†

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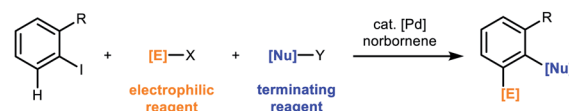
We herein report a denitrogenative palladium-catalyzed cascade for the modular and regioselective synthesis of polysubstituted fluorenes. Hydrazone facilitates the Pd(II) to Pd(IV) oxidative addition in a Catellani pathway and is also the methylene synthon in the proposed reaction. Aryl iodides and 2-bromoarylaldehyde hydrazones undergo a norbornene-controlled tandem reaction sequence to give a broad scope of fluorenes in the presence of a palladium catalyst. The method described is scalable and adaptable to a three-component reaction with *in situ* generation of the hydrazone group. Preliminary mechanistic investigations have been conducted.

Introduction

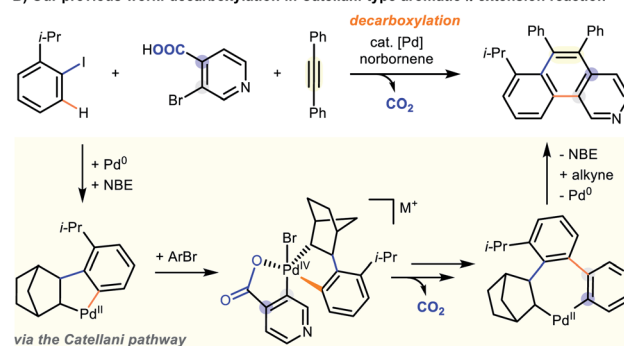
Regioselective functionalization of organic molecules is one of the most important, yet challenging objectives in modern synthetic organic chemistry.¹ In this regard, the Catellani reaction, which was discovered by the Catellani group in 1997,² is a powerful and versatile tool for constructing polysubstituted arenes in a regioselective fashion *via* palladium/norbornene cooperative catalysis.³ The transformation is a tandem difunctionalization of aryl iodides which installs nucleophile ([E]-X) and electrophile ([Nu]-Y) at both *ipso*- and *ortho*-positions (Fig. 1A).^{2,3} After 20 years of advancements, a large number of chemical transformations have been successfully incorporated into the Catellani reaction manifold, which includes Mizoroki–Heck reaction,^{2,4} Sonogashira coupling,⁵ Suzuki coupling,⁶ enolate coupling,⁷ amination,⁸ borylation,⁹ cyanation,¹⁰ direct C–H arylation,¹¹ thiolation¹² and others.¹³ Recent contributions in this field have also revealed that Catellani-type reactions can be initiated by Pd(II) species with starting materials other than aryl iodides.¹⁴ Amongst the Pd(0) or Pd(II)-initiated Catellani cycles, directing/chelating groups were often used to facilitate the Pd(II)–Pd(IV) oxidative addition or to affect selective arene C–H activation.¹⁵ Nevertheless, these assisting groups often remain in the product structure and may not always be a subsequent synthetic handle for future derivatizations. In order to address this pitfall, our group have recently

demonstrated the utilization of a deciduous carboxyl group¹⁶ to facilitate the Pd(II)/(IV) oxidative addition in Catellani-type aromatic π -extension reactions (Fig. 1B).¹⁷ As part of our

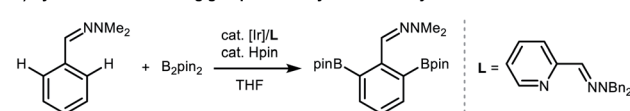
A) The Catellani reaction



B) Our previous work: decarboxylation in Catellani-type aromatic π -extension reaction



C) Hydrazone as a directing group in Ir-catalyzed C–H diborylation



D) This work: denitrogenation in regioselective synthesis of fluorenes

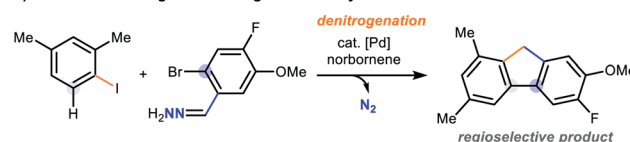


Fig. 1 (A) A typical Catellani reaction; (B) previous work: decarboxylative aromatic π -extension reactions; (C) hydrazone as a directing group in Ir-catalyzed C–H borylations; (D) this work: Pd-catalyzed norbornene-mediated denitrogenative synthesis of fluorenes.

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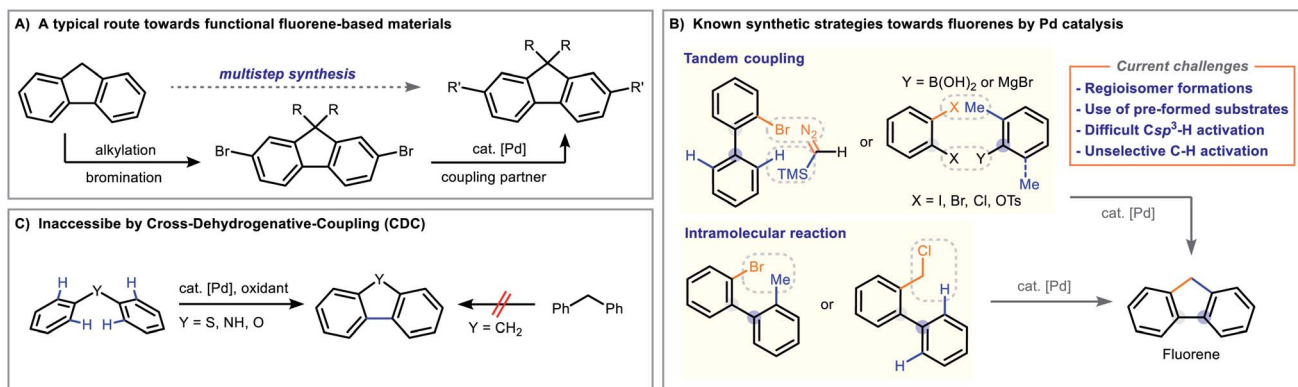


Fig. 2 Approaches and difficulties of fluorene syntheses; (A) traditional multistep synthesis of fluorenes; (B) Pd-catalyzed tandem or intramolecular synthesis of fluorenes; (C) lack of directing abilities of methylene group in fluorene.

continuing efforts in Pd/norbornene chemistry, we aim to explore new methods to access other chemical classes. Hydrazones have been reported to be a useful directing group in Pd-, Rh- or Ir-catalyzed reactions (Fig. 1C),¹⁸ and we sought to adopt it as an assisting group to facilitate the heterobiaryl formation in the Catellani cycle. During our investigations, we found that aryl iodides reacted with 2-bromoarylaldehyde hydrazone to give fluorenes under typical Catellani reaction conditions. Herein we report the development and results of a novel denitrogenative palladium-catalyzed cascade for the modular and regioselective synthesis of fluorenes (Fig. 1D).

Although fluorene and its derivatives are ubiquitous structural motifs in light-emitting optoelectronics,¹⁹ organic semiconductors,²⁰ nanostructures,²¹ functional polymers,^{20c,22} chemosensors^{19a,23} and bioactive compounds,²⁴ we identified a multitude of challenges on their syntheses based on literature precedents. Traditional synthesis of substituted fluorenes mostly rely on the post-functionalization of 9H-fluorene via lengthy sequences (Fig. 2A),^{20a} while transition metal-catalyzed reactions have also been developed to efficiently prepare fluorenes in one pot (Fig. 2B).²⁵ Construction of the methylene group employs intramolecular direct C sp³-H activation or cleavage of a C sp³-X bond, but these biaryl substrates require pre-activation and inherently offset the methods' accessibility and scope.^{20c,26} These pre-functionalized substrates are typically prepared in multiple synthetic steps and the C9 (methylene) position is often substituted with functional groups, which cannot be readily converted into other moieties, such as alkyl chains that are important for liquid crystal formation.^{19a,27} Recently, impressive carbenoid cross-coupling strategies have been disclosed by the groups of Wang, Hu and others.²⁸ However, the formation of regioisomers was still possible due to the unselective oxidative addition of C-Br/Cl bond and C-H activation. Although cross-dehydrogenative coupling (CDC) is useful in the preparation of heterocycles (Fig. 2C),²⁹ it is not applicable for accessing fluorenes owing to the lack of directing abilities of the methylene group in the diarylmethane scaffold.

Results and discussion

At the outset of our investigation, we found that the reaction between 2-bromobenzaldehyde hydrazone (2a) and 2-

iodotoluene has given fluorene 3a in 38% yield in the presence of a Pd(OAc)₂/PPh₃ catalyst and norbornene (Table 1, entry 1). An optimization study of reaction parameters was then undertaken with a survey of phosphine ligands, solvents bases and stoichiometry of reagents. Selected entries of our optimization have been shown in Table 1 (please see Tables S1–S3 in ESI† for detailed optimization data). Amongst the trialkyl or triaryl

Table 1 Selected entries for reaction optimization^a

Entry	Ligand	Base	Solvent	% Yield ^b
1	PPh ₃	K ₂ CO ₃	Toluene	38
2	PCy ₃	K ₂ CO ₃	Toluene	57
3	PCyPh ₂	K ₂ CO ₃	Toluene	74
4	P(4-OMeC ₆ H ₄) ₃	K ₂ CO ₃	Toluene	43
5	cataCXium A	K ₂ CO ₃	Toluene	13
6	XPhos	K ₂ CO ₃	Toluene	37
7	PPh ₂ -DavePhos	K ₂ CO ₃	Toluene	45
8 ^c	DPPF	K ₂ CO ₃	Toluene	31
9	PCyPh ₂	Cs ₂ CO ₃	Toluene	73
10	PCyPh ₂	Na ₂ CO ₃	Toluene	5
11	PCyPh ₂	K ₂ CO ₃	DMF	80
12	PCyPh ₂	K ₂ CO ₃	NMP	78
13	PCyPh ₂	K ₂ CO ₃	1,4-Dioxane	76
14	PCyPh ₂	K ₂ CO ₃	CH ₃ CN	35
15 ^d	PCyPh ₂	K ₂ CO ₃	DMF	0

Ligands: PPh₂-DavePhos, XPhos, DPPF, cataCXium A.

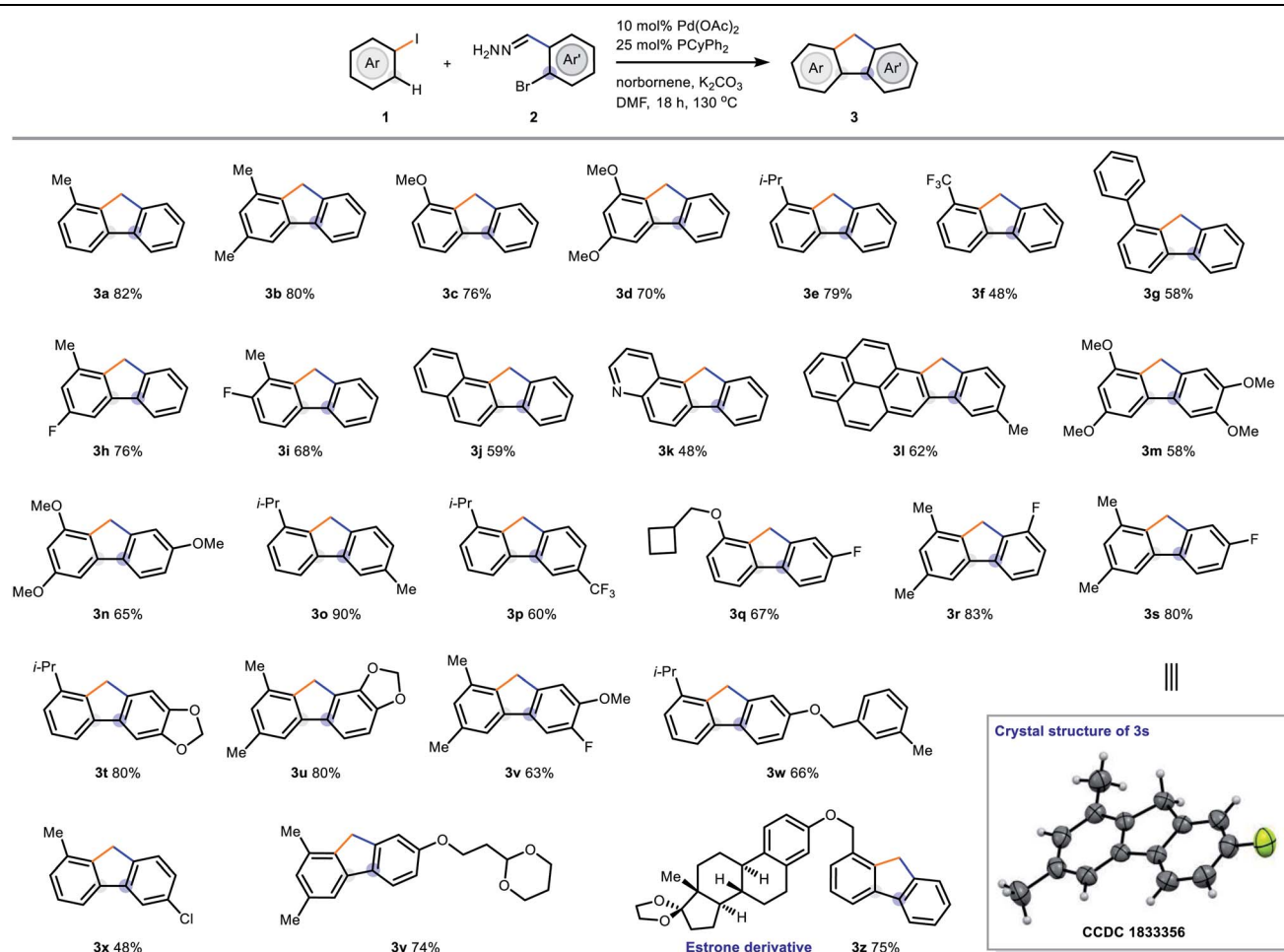
^a Reaction conditions: Pd(OAc)₂ (10 mol%), ligand (25 mol%), 2-iodotoluene (0.2 mmol), (2-bromobenzaldehyde)hydrazone (0.24 mmol), norbornene (0.3 mmol), base (0.6 mmol), solvent (0.1 M), 130 °C for 18 h under N₂. ^b Calibrated GC-FID yields. ^c 12.5 mol% of DPPF was used. ^d Reaction without norbornene.



monophosphine ligands screened (entries 1–4), PCyPh₂ provided the highest product yield (74%, entry 3). Either increasing or decreasing the electron richness of the phosphorus donor led to a drop in product yield. Bulky cataCXium A and other biaryl phosphine ligands showed inferior activity in this comparison (entries 5–7). Bidentate phosphine such as DPPF was not suitable for this reaction (entry 8). Cs₂CO₃ gave a similar yield to that of K₂CO₃ and the later one was chosen for further study because of its economical attractiveness (entry 3 vs. 9). Gratifyingly, the product yield was further increased to 80% when DMF was employed as solvent (entry 3 vs. 11). Other solvents gave comparable performances to that of toluene (entries 12–13), except acetonitrile (entry 14). A control experiment without norbornene was carried out and desired product was not observed (entry 15).

Having identified an optimal reaction conditions, we then studied the reaction scope of our reaction. Aryl iodides with different electron richness and steric bulkiness were first tested (Table 2, **3a–3l**, **3q**). Electron-rich and – neutral aryl iodides were converted to the desired products in 68–82% isolated yields (**3a–3e**, **3h–3i**). However, substrates bearing an electron-

withdrawing group such as –CF₃ caused a drop in yield and **3f** was isolated in 48% yield. Aryl iodides with sterically hindered *ortho*-substituents such as phenyl or isopropyl groups underwent the transformation smoothly to afford the corresponding fluorenes **3g** and **3t** in moderate-to-good yields. Heteroatom-containing and polyaromatic substrates were tolerated (**3j–3l**) and it is worth to mention that polyaromatic hydrocarbons (PAHs) contribute important properties in light-emitting devices and fluorophores.³⁰ We next turned our attention to the scope of aryl hydrazones **2**. We were pleased that the transformations proceeded efficiently to give multi-substituted fluorenes **3l–3z** with complete regioselectivity (up to 90% yield). The structure of **3s** was determined by single crystal X-ray analysis.³¹ Aryl hydrazones containing electron-donating and –withdrawing groups were applicable substrates (**3m–3s**). Polycyclic fluoreno[1,3]dioxoles **3t** and **3u** were isolated in 80% yield. The alkyl aryl ether (**3w**) and acetal group (**3y**) can be readily transformed into phenol and aldehyde, respectively. Chloro group (**3x**) was compatible and provides access to further functionalizations by palladium-catalyzed cross-couplings.³² Estrone-derived aryl iodide also reacted under the standard

Table 2 Substrate scope^a

^a Reaction conditions: Pd(OAc)₂ (10 mol%), PCyPh₂ (25 mol%), aryl iodide (0.2 mmol), **2** (0.24 mmol), norbornene (0.3 mmol), K₂CO₃ (0.6 mmol), DMF (0.1 M), 130 °C for 18 h under N₂. Isolated yields were reported.

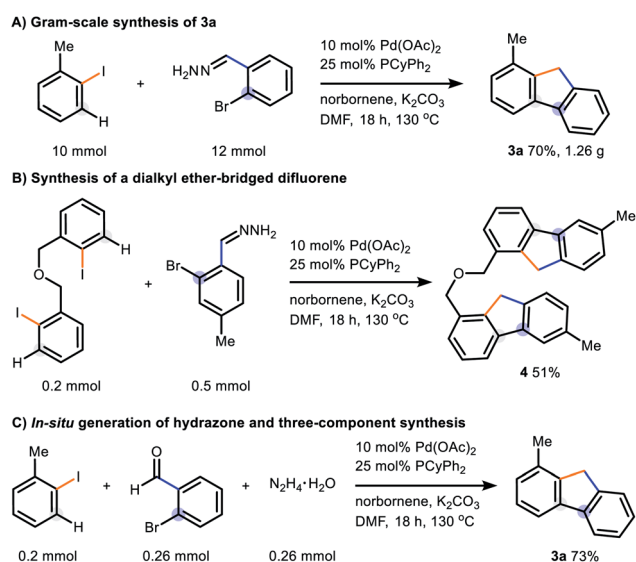


conditions to provide **3z** in 75% isolated yield. Interestingly, reaction of aryl iodides without *ortho*-substituents, or with small *ortho*-substituents such as fluorine, gave norbornene-embedded heptagon compounds,³³ in which it showed that the steric hindrance exerted by the *ortho*-substituents is critical for the extrusion of norbornene and thus the five-membered ring formation. Further study of this outcome is currently underway in our laboratory.

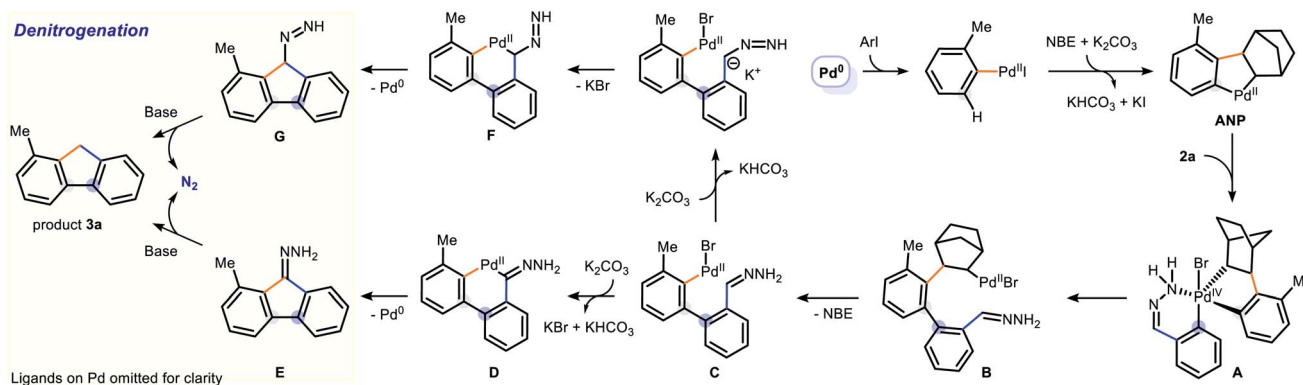
To demonstrate the synthetic utility of our method in a wider scope, we carried out a gram-scale synthesis and 1.26 g of fluorene **3a** was successfully obtained under standard reaction conditions (Scheme 1A). A diiodide substrate underwent the transformation successfully to form a dialkyl ether-linked difluorene **4** in 51% yield (Scheme 1B). To circumvent the access of hydrazones in this tandem reaction, we sought to adapt our system to a three-component reaction with *in situ* generation of the aryl hydrazone using 2-bromobenzaldehyde and hydrazine (Scheme 1C). All commercially available materials were employed and the desired product **3a** was given in

73% isolated yield, in which the yield only decreased slightly in comparison to entry **3a** of Table 2.

A mechanistic proposal of our reaction is illustrated in Scheme 2. The cascade initiates with the oxidative addition of 2-iodotoluene to Pd(0), followed by a migratory insertion of NBE and palladation of the *ortho*-C–H bond to give the ANP (aryl-norbornene palladacycle). Based on our previous works and literature reports, it is reasonable to hypothesize the formation of a Pd(IV) intermediate **A** from ANP.^{3,17} The hydrazone chelates to the Pd(II) and assists with the oxidative addition of **2a** by allowing the C–Br bond to sit near the Pd centre. The reductive elimination of **A** generates the biaryl palladium(II) species **B** in a regioselective fashion and subsequent β -carbon elimination of norbornene gives the key intermediate **C**. We have observed a trace amount of intermediate **E** on GC-MS during the optimization studies, which suggests a possible C–H activation on the hydrazone to form palladacycle **D**. The Wolff–Kishner reduction of **E** gives the final product **3a**.³⁴ Alternatively, another possible pathway could be similar to the cross-coupling of Umpolung aldehydes, which were very recently reported by Li and co-workers.³⁵ The deprotonation of hydrazone forms a carbon nucleophile, which upon substitution with the bromide would yield palladacycle **F**. Reductive elimination of **F** regenerates Pd(0) and affords intermediate **G**, which undergoes denitrogenation to give **3a** under a basic condition. Although a deuterium labelling study was attempted (Scheme S1[†]), the results were not conclusive due to the H/D exchange nature of the C9-proton ($pK_a = 22.6$ in DMSO for fluorene) under basic conditions.³⁶ The Wolff–Kishner reduction was also tested by subjecting hydrazone **5** under standard reaction conditions in the absence of palladium catalyst (Scheme 3A) and 50% yield of fluorene **6** was obtained. However, the addition of 10 mol% Pd catalyst to the system increased the product yield of **6** to 73%, in which it is possible that the reduction could be assisted by a palladium process. Control experiments regarding the reaction pathway were carried out (Scheme 3B). An *N*-tosyl hydrazone **7** was subjected to the reaction system but no desired product was obtained, indicating the absence of a carbene migratory insertion within intermediate **C**. When the ketone-derived hydrazone **8** was used, no corresponding product was detected, in which it

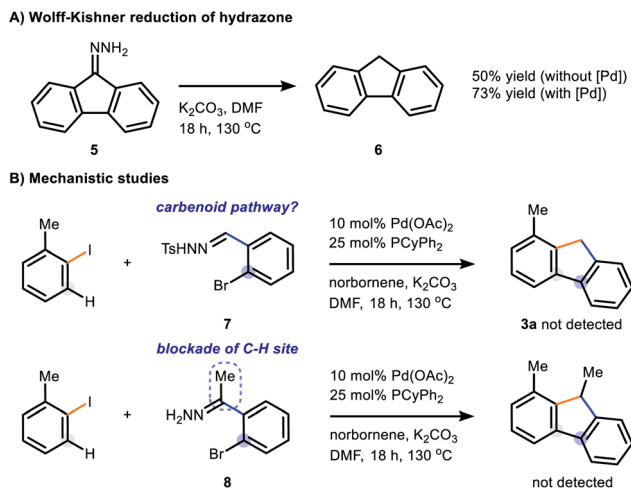


Scheme 1 Synthetic utilities of our reaction; (A) scalability of our reaction; (B) reaction of a diiodide substrate; (C) *in situ* generation of hydrazone in a three-component reaction.



Scheme 2 Mechanistic proposal.





Scheme 3 (A) Wolff-Kishner reaction of 9-fluorenone hydrazone under standard conditions as shown in Table 2, [Pd] = 10 mol% Pd(OAc)₂ and 25 mol% PCyPh₂; (B) mechanistic studies.

reveals the importance of the C–H site for intramolecular C–H activation by the Pd(II) centre.

Conclusions

In summary, a denitrogenative palladium-catalyzed cascade has been developed to allow for facile assembly of polysubstituted fluorenes. Hydrazone was utilized as a deciduous chelating group to facilitate the Pd(II)/Pd(IV) oxidative addition in a Catellani cycle while it also served as a methylene synthon for the fluorene C-9 carbon. This modular synthesis exhibited complete regioselectivity and provided fluorenes with various substitution patterns in good-to-excellent product yields. *In situ* generation of hydrazones from aldehydes has also been illustrated in a three-component cross-coupling reaction. We believe that the reaction scope, as well as the use of a commercial catalyst and easily available reactants, would render our method attractive and versatile for synthetic applications in material science, medicinal chemistry and organic chemistry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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