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Synthesis of Fluoren-9-ones and Ladder-Type Oligo-*p*-phenylene Cores via Pd-Catalyzed Carbonylative Multiple C–C Bond Formation

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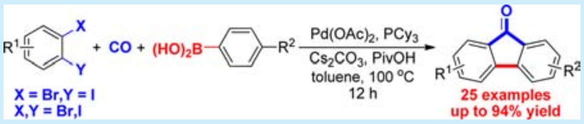
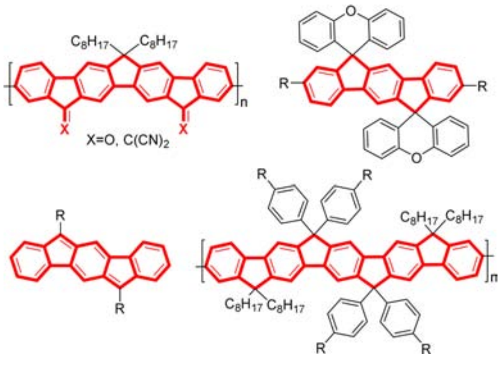
Supporting Information



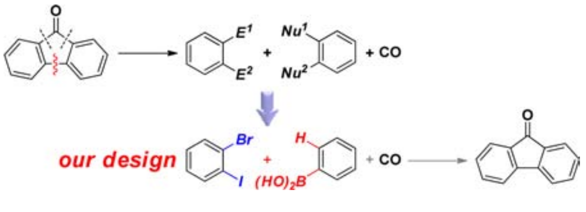
ABSTRACT: A new route to various substituted fluoren-9-ones has been developed via an efficient Pd-catalyzed carbonylative multiple C–C bond formation. Under a CO atmosphere, using commercially available aryl halides and arylboronic acids as substrates, this three-component reaction proceeded smoothly in moderate to excellent yields with good functional-group compatibility. The mechanistic investigations suggested a sequential process for the reaction that forms *o*-bromobiaryls in the first stage followed by a cyclocarbonylation reaction. This chemistry has been successfully extended to construct ladder-type oligo-*p*-phenylene cores.

Fluoren-9-one and its derivatives are considered as a sort of privileged structure which constitute the central core of a variety of compounds exhibiting extraordinary biological and pharmaceutical activities as well as optical and electronic properties.[1] Especially, with the development of organic semiconductive materials during the past four decades, research on fluorene-based organic photoelectric materials has evolved as a lively field of activity, owing to their intense blue photo- and electroluminescence, liquid crystalline properties, etc.[1d,f,g,2] Tremendous scientific effort has been devoted to their possible application in the field of organic electronics such as organic and polymer light-emitting diodes, bulk heterojunction solar cells, photochemical sensitizers, etc. (Scheme 1).[1g,3] Fluoren-9-one is the most commonly used precursor, which gives great diversity in fluorene-based molecular architectures and allows fine-tuning of the desirable properties.[4] Therefore, it is essential to construct the fluoren-9-one building blocks. Taking the structure of the fluoren-9-one core into consideration, the key for its construction relies on three single C–C bonds connecting two aryls and one carbonyl group. Except for the oxidation of 9*H*-fluorenes or 9*H*-fluoren-9-ol,[5] other reported methods were more or less focused on forming those three single bonds.[6,7] However, to date, only one or two of those single bonds were constructed in one synthetic process, and more functionalized precursors were required, which might restrict the commercial source. Therefore, it would be appealing to construct those three single bonds directly by one protocol using only simple aryl compounds combined with CO as the suitable starting materials. Herein, we disclose the first report on the Pd-catalyzed carbonylative cross-coupling of aryl dihalides with arylboronic acids, which forms three single C–C bonds in one operation to construct fluoren-9-one. In our design, *o*-dihaloarene acted as the nucleophile while arylboronic acid as the electrophile, with CO as the carbonyl source, and finally, fluoren-9-one building blocks were synthesized in a convenient mode (Scheme 2).

Scheme 1. Classic Molecule Materials Based on Fluorene Frameworks



Scheme 2. Our Design To Construct Fluoren-9-one Building Blocks



o-Bromoiodobenzene was selected in our initial study. When it was treated with phenylboronic acid under a CO atmosphere, to our delight, in the presence of $Pd(OAc)_2/PCy_3$ as the catalyst, and Cs_2CO_3 as the base in toluene, the reaction gave the corresponding fluoren-9-one in 35% yield. We subsequently explored the effect on the reaction yield of other variations such

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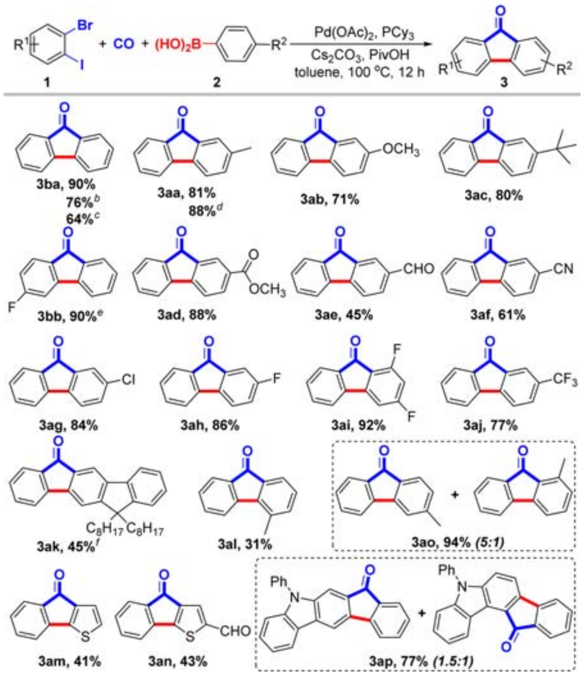
as temperature, Pd catalyst precursors, solvents, ligands, use of various bases, etc. The details were summarized in the Supporting Information (Table 1). The optimum reaction conditions thus far include employing 1 atm of carbon monoxide, 1.0 equiv of *o*-bromoiodobenzene (0.5 mmol), 1.2 equiv of phenylbronic acid, 5 mol % of Pd(OAc)$_2$, 10 mol % PCy$_3$, 3.0 equiv of anhydrous Cs$_2$CO$_3$, and 1.0 equiv of PivOH in toluene (3 mL) at 100 °C for 12 h. This procedure provided fluoren-9-one (**3ba**) in a 90% yield.

Under the optimized reaction conditions, a variety of arylboronic acids were employed to further investigate the scope of this new catalyst system. As demonstrated in Scheme 3, this reaction had good functional group tolerance. All arylboronic acids proceeded smoothly to afford corresponding products in moderate to excellent yields. Arylboronic acids bearing electron-withdrawing groups including −F (**3bb**, **3ah**−**3ai**), −Cl (**3ag**), −CF$_3$ (**3aj**), −CN (**3af**), and −COOMe (**3ad**) were well tolerated and gave good to excellent yields (61%−92%). However, in the case of the −CHO group, a low yield was obtained (45% for **3ae** and 43% for **3an**, repectively). Electron-donating groups such as −Me (**3aa**), OMe (**3ab**), and −*t*-Bu (**3ac**) also afforded the desired products in satisfactory yields. Meaningfully, functional groups such as −CHO, −CN, -F, −*t*-Bu, etc. always have the potential to improve the properties of materials when further derived.[8] For example, the existence of the formyl functional group offered the opportunity for further utility in Dye Sensitized Solar Cells (DSSCs).[9] Fluoro-substituted aryl groups usually were beneficial for improving fluorescence quantum efficiency in luminescent materials,[10] and the *tert*-butyl group helps to enhance the solubility of materials, increase steric hindrance to avoid congregating of molecules, etc.[11] These experimental results indicated that there was only a weak electronic effect in this reaction. In contrast, steric hindrance has a great influence on this transformation, and a relatively low yield was obtained (**3al**). A similar steric effect was also observed in the reaction of *meta*-substituted arylboronic acids, which favored the less hindered isomer parts (**3ao**, **3ap**). However, interestingly, two isomers of **3ao** and **3ap** were easily separated and would be beneficial to the study on the structure−property relationship of materials. **3ak** was a highly fluorescent indenofluorenone building block and has been applied in the field of optoelectronic materials[12] By this Pd-catalyzed transformation, **3ak** was produced in 45% yield. We have also attempted to employ thiopheneboronic acids in our method. The yields of products **3am** and **3an** were relatively, low but they were difficult to synthesize in common methods.[13] On the other hand, this Pd reaction did not appear to be affected by the presence of substituents at the C-3 and C-4 position of *o*-bromoiodobenzenes (**3bb**, **3aa**).

Scheme 3. Synthesis of Fluoren-9-ones via Palladium Catalyzed Three-Component Carbonylative Reaction[a]

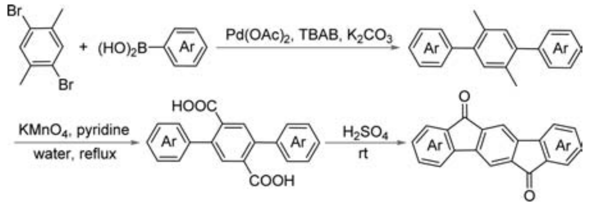


[a]Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), Pd(OAc)$_2$ (5 mol %), PCy$_3$ (10 mol %), Cs$_2$CO$_3$ (3.0 equiv), PivOH (1.0 equiv), toluene (3 mL), 100 °C, 12 h, CO (1 atm). Isolated yields. [b]**1** (1,2-dibromobenzene). [c]**1** (1,2-diiodobenzene). [d]**1** (2-bromo-1-iodo-4-methylbenzene). [e]**1** (1-bromo-4-fluoro-2-iodobenzene). [f]**2** (2-(9,9-dioctyl-9*H*-fluoren-2-yl)-1,3,2-dioxaborinane).

In the above-mentioned reactions, *o*-bromoiodobenzene was adopted as an annulation partner to increase the reaction selectivity. However, this Pd reaction was also effective for 1,2-dibromo- and 1,2-diiodobenzene (**3ba**, **3ba**). Under the standard reaction conditions, phenylboronic acid produced the desired fluorenone in a slightly lower yield of 76% and 64%, respectively.

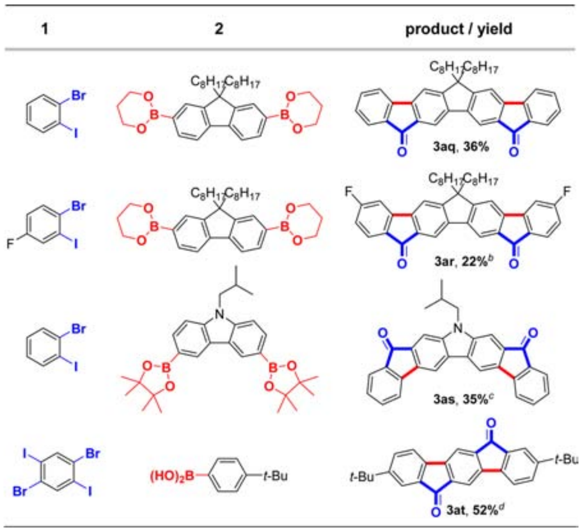
Linear ladder-type oligo-*p*-phenylenes, which formally consist of several "'linearly overlapping"' fluorenes, served as an even better *π*-conjugated center in the design of a two-photon active chromophore, owing to their enhanced *π*-conjugation. They have been well studied in several reports and accepted as an efficient platform for construction of a planar and rigid *π*-conjugated system, which may provide a high two-photon absorption (TPA) response with enhanced emission, and increased thermal and chemical stabilities, because a simultaneous rupture of at least two bonds is necessary for complete scission of a ladder structure.[1g,3f−k,14] However, the traditional synthetic routes for these types of compounds were multistep and laborious as exemplified in Scheme 4.[14g] Therefore, a more challenging double annulation of this Pd method was attempted using a double arylboronic acid ester or 1,4-dibromo-2,5-diiodobenzene (Scheme 5). Delightedly, some linear ladder-type oligo-*p*-phenylene structures (**3aq**, **3ar**, **3as**, **3at**) were prepared in acceptable yields. Thus, this method indicated its potential for the synthesis of a wide variety of ladder-type poly-*p*-phenylenes, which offered more possibilities to improve the performance of materials.

Scheme 4. Traditional Approach for the Synthesis of Indenofluorenedione



Based on the position of the substituents in products, we speculated that this Pd-catalyzed carbonylative multiple C−C bond formation might undergo a sequential process. The first step is Suzuki coupling of the more reactive C−I bond with

Scheme 5. Synthesis of Linearly Overlapping Fluorenes by the Palladium-Catalyzed Double Annulation Reaction[a]



[a] Reaction conditions: **1** (0.5 mmol), **2** (0.3 mmol), Pd(OAc)$_2$ (5 mol %), PCy$_3$ (10 mol %), CO (1 atm), Cs$_2$CO$_3$ (3.0 equiv), PivOH (1.0 equiv), toluene (3 mL), 100 °C, 12 h. Isolated yields. [b] **1** (1-bromo-4-fluoro-2-iodobenzene). [c] **2** (9-isobutyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole, 0.25 mmol), **1** (1.0 mmol), Pd(OAc)$_2$ (20 mol %), PCy$_3$ (40 mol %). [d] **1** (0.25 mmol), **2** (0.6 mmol), Pd(OAc)$_2$ (10 mol %), PCy$_3$ (20 mol %), 90 °C.

arylboronic acid to generate *o*-bromobiaryls, followed by an intramolecular C−H carbonylation. To acquire further insight into the mechanism, we monitored the reaction between **1a** and **2d** by *in situ* IR under the standard conditions. The profiles of relative absorbance versus time for individual species are shown in Figure 1. The kinetic profiles (Figure 1) demonstrated that a new peak at 1278 cm^{-1} increased at the beginning of the reaction and then declined after 3 h. This component was assigned to be **3u** compared with the authentic sample (see Supporting Information, Figure 1). Meanwhile, the product **3ad** (peak at 1255 cm^{-1}) was generated gradually. The corresponding change trend was presented in the 2D-kinetic profile in Figure 1B; **3u** underwent an accumulation and decrease process simultaneously with the generation of product (**3ad**).

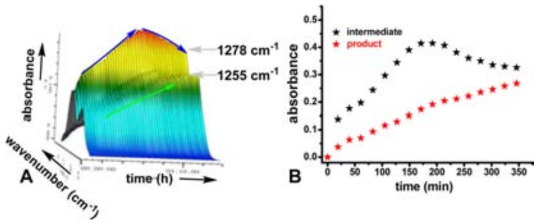
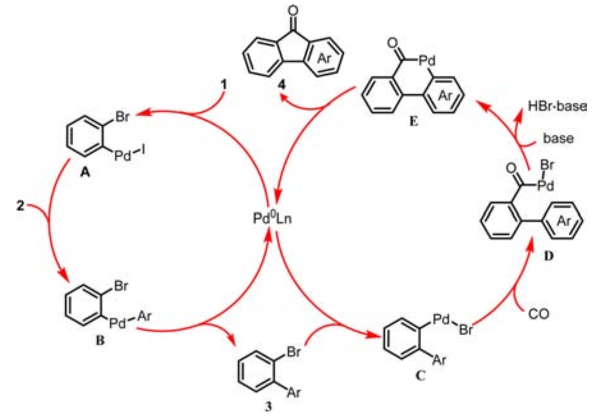


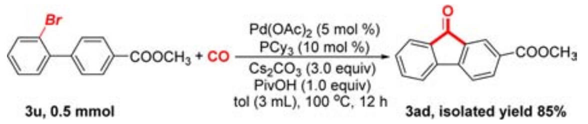
Figure 1. (A) The 3D-FTIR profile of *o*-bromoiodobenzene (0.5 mmol) reacted with (4-(methoxycarbonyl)phenyl)boronic acid (0.6 mmol) under standard conditions. (B) The 2D-kinetic profile of the reaction of *o*-bromoiodobenzene (0.5 mmol) reacted with (4-(methoxycarbonyl)-phenyl)boronic acid (0.6 mmol) under standard conditions monitored by in situ IR.

A putative reaction mechanism was then proposed in Scheme 6. In the first stage, **1** coupled with **2** to generate **3**. Subsequently, oxidative addition of species **3** to Pd(0) formed intermediate **C**, followed by insertion of the coordinated CO into the C−Pd bond to produce the acylpalladium intermediate **D**, which further eliminated a molecule of HBr to convert to intermediate **E** followed by reductive elimination to the product **4** with simultaneous regeneration of the Pd(0) catalyst. Conclusive evidence for the suggested mechanism was provided by the isolation of intermediate **3u**, followed by heating of **3u** under standard conditions leading to the formation of **3ad** in 85% yield (Scheme 7).

Scheme 6. Proposed Mechanism



Scheme 7. Reaction of 3u with CO Under Standard Conditions



In summary, we developed a direct, highly efficient approach for the construction of fluorenones and ladder-type oligo-*p*-phenylene cores via a Pd-catalyzed carbonylative multiple C−C bond formation by using simple and commercially available *o*-dihaloarene combined with arylboronic acid as the substrate under CO. This new strategy, carbonylation with CO coupled with a one-pot, multistep reaction, will certainly attract the attention of organic chemists interested in this class of compounds because of its atom and step economy. Noteworthy is that, by extension, a series of fluoren-9-ones with various substituents and π-conjugated expanded systems were obtained in one step, indicating a promising future in the field of medicinal chemistry and especially material science. Studies on the application of π-conjugated expanded fluorenone systems in organic photoelectric materials are in progress in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental procedures, synthesis characterization details, and copies of ^{1}H, ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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