Synthesis of Fluoranthene Derivatives via Tandem Suzuki-Miyaura and Intramolecular C-H Arylation Reactions under both Homogeneous and Heterogeneous Catalytic Conditions

Sujit Pal,‡ † Önder Metin,*§ and Yunus E. Türkmen*‡ †

†Department of Chemistry, Faculty of Science, and ‡UNAM — National Nanotechnology Research Center and Institute of Materials Science and Nanotechnology, Bilkent University, 06800 Ankara, Turkey
§Department of Chemistry, Faculty of Science, Atatürk University, 25240 Erzurum, Turkey

ABSTRACT

A catalytic method for the synthesis of substituted fluoranthenes that operates via tandem Suzuki-Miyaura and intramolecular C-H arylation reactions is reported. The overall reaction sequence works effectively with homogeneous catalysis using Pd(dppf)Cl₂ as well as heterogeneous catalysis using rGO-CuPd nanocatalysts with low catalyst loadings. High functional group tolerance was observed under both catalytic conditions where arylboronic acids and esters having electron-withdrawing and donating substituents afforded fluoranthene products in good yields (up to 78%). Moreover, rGO-CuPd nanocatalysts are demonstrated to be reusable by preserving almost 90% of their initial activity after the third cycle.
INTRODUCTION

Fluoranthenes represent an important subclass of polycyclic aromatic hydrocarbons (PAHs) with a broad range of attractive applications.\(^1\) A number of fungal natural products have fluoranthene core in their structures such as hortein\(^{2a}\) (1) and daldinone E\(^{2b}\) (2) among others, some of which exhibit important biological activities (Figure 1).\(^2\) Fluoranthenes have also found widespread applications in materials science, particularly in the area of organic electronics.\(^3\) For instance, FLUN-550 (3) was introduced by Goel, Mitra and co-workers in 2014 as a fluoranthene-based fluorescent probe for selective staining of intracellular lipid droplets.\(^4\) Structurally related diacenaphthylene-fused benzodithiophenes (4) have recently been developed by Yang, Li and co-workers, and their field-effect mobilities have been investigated (Figure 1).\(^5\)

![Figure 1](image.png)

Figure 1. Examples of important fluoranthene analogues

Among the methods available for the synthesis and derivatization of fluoranthenes, Diels-Alder reaction has been the most commonly utilized method,\(^3a-c,3e,4,6\) whereas transition-metal catalyzed reactions and various other cyclization strategies have also been employed.\(^3d,5,7\) In 2009, Scott and co-workers reported an effective method for the synthesis of fluoranthenes starting from 1,8-
dichloronaphthalenes and arylboronic acids in the presence of a homogeneous Pd catalyst. However, this reaction requires high catalyst loading (20 mol% Pd$_2$(dba)$_3$) and high reaction temperatures (155-175 °C). Total synthesis of the natural product benzo[j]fluoranthene-4,9-diol was accomplished by Dallavalle and co-workers in 2013 wherein the fluoranthene core was assembled by a McMurry ring closure. More recently, Manabe and co-workers developed an elegant Pd-catalyzed method that enables three-step synthesis of fluoranthenes via inter- and intramolecular C-H arylation reactions. During the course of our studies on 1,8-diarylnaphthalenes, we have observed that monoaryl as well as symmetrical and unsymmetrical diarylnaphthalenes could be obtained selectively via Suzuki-Miyaura reaction using tetrakis(triphenylphosphine)palladium(0) (Pd(PPh$_3$)$_4$) catalyst starting from 1,8-dioiodonaphthalene (5). On the other hand, using a more active Pd catalyst, Pd(dppf)Cl$_2$, led to the formation of significant amounts of fluoranthene side-products, which prompted us to investigate this transformation in detail. Herein, we report a highly effective method for the synthesis of substituted fluoranthenes that can operate under both homogeneous and heterogeneous catalytic conditions.

**RESULTS AND DISCUSSION**

We initiated our study by examining the reaction between 1,8-dioiodonaphthalene (5) and 4-fluorophenylboronic acid (6a) in the presence of homogenous Pd catalysts (Table 1). As aforementioned, the Suzuki-Miyaura monoarylation product was obtained as the major product when Pd(PPh$_3$)$_4$ was used as the catalyst with no formation of fluoranthene 6b (entry 1). Pleasingly, Pd(dppf)Cl$_2$ proved to be an effective catalyst for the desired transformation when used in 5 mol% catalyst loading. Among the carbonate and acetate bases screened, KOAc gave the highest yield of fluoranthene 6b in DMSO at 90 °C (71%, entries 2-6). Inferior results were obtained when KO'Bu, CsF and NaOH were examined as bases (entries 7-9). With KOAc selected as the optimal base, we then performed a solvent screening. While DMF was completely ineffective under the same reaction conditions, we observed significant improvement in yield when DMSO was used as the solvent (76%, entry 7). Further optimization of the reaction conditions revealed that an increase in temperature to 100 °C resulted in an increase in yield to 81% (entry 8). With these optimized reaction conditions, we were able to achieve high yields of substituted fluoranthenes under both homogeneous and heterogeneous catalysis conditions.
conditions (entry 10), CH$_3$CN, dioxane and DMA afforded the desired product 6b, albeit in lower yields (31, 48 and 38%, respectively, entries 11-13). Finally, Pd(OAc)$_2$/P$^i$Bu$_3$:HBF$_4$ and Pd$_2$(dba)$_3$/P$^i$Bu$_3$:HBF$_4$ combinations were found to be catalytically less active compared to Pd(dppf)Cl$_2$ (entries 14 and 15).

**Table 1. Optimization Studies using Homogeneous Catalysts**

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>base</th>
<th>solvent</th>
<th>yield (%)$^b$</th>
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<td>1</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>KOAc</td>
<td>DMSO</td>
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</tr>
<tr>
<td>2</td>
<td>Pd(dppf)Cl$_2$</td>
<td>K$_2$CO$_3$</td>
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<td>10</td>
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<tr>
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<td>Cs$_2$CO$_3$</td>
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<td>4</td>
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<td>Na$_2$CO$_3$</td>
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<td>28</td>
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<tr>
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<td>DMSO</td>
<td>71</td>
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<td>Pd(dppf)Cl$_2$</td>
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<td>DMSO</td>
<td>69</td>
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<td>7</td>
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<td>KO'Bu</td>
<td>DMSO</td>
<td>&lt;5</td>
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<td>KOAc</td>
<td>DMA</td>
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<td>14$^d$</td>
<td>Pd(OAc)$_2$/ P$^i$Bu$_3$:HBF$_4$</td>
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<td>DMSO</td>
<td>21</td>
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<tr>
<td>15$^e$</td>
<td>Pd$_2$(dba)$_3$/ P$^i$Bu$_3$:HBF$_4$</td>
<td>KOAc</td>
<td>DMSO</td>
<td>14</td>
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$^a$0.13 mmol of 5, 0.15 mmol of 6a, 0.52 mmol of base, 5 mol% of Pd catalyst, 90 °C, N$_2$, 24 h. $^b$Isolated yields. $^c$T = 80 °C. $^d$P$^i$Bu$_3$:HBF$_4$:Pd(OAc)$_2$ = 2:1. $^e$P$^i$Bu$_3$:HBF$_4$:Pd$_2$(dba)$_3$ = 4:1. Abbreviations: DMA, N,N-dimethylacetamide; dppf, 1,1'-bis(diphenylphosphino)ferrocene; dba, dibenzylideneacetone.
Having successfully optimized the fluoranthene synthesis in the presence of homogeneous palladium catalysts, we then turned our attention to the utilization of a heterogeneous catalyst for this transformation, considering the advantages of heterogeneous catalysts over homogenous ones. As the classical heterogeneous catalysts have limited surface area resulting in low activity, nanocatalysts emerged as highly efficient catalysts for various organic reactions in recent years owing to their high surface to volume ratio.\textsuperscript{11} In this respect, Metin research group has demonstrated that bimetallic Pd nanoparticles (NPs) assembled on reduced graphene oxide (rGO) were highly efficient catalysts in a variety of organic transformations.\textsuperscript{12} Especially, rGO-assembled CuPd alloy NPs (rGO-CuPd) were shown to be highly efficient heterogenous catalysts in Sonogashira cross-coupling reactions.\textsuperscript{12a} By the motivation of these promising results, we selected rGO-CuPd nanocatalyst as a heterogeneous catalyst to be tested in this transformation.\textsuperscript{13} We first conducted optimization experiments depending on various parameters in the presence of rGO-CuPd nanocatalyst (Table 2). As can be seen in Table 2, rGO-CuPd nanocatalyst provided the highest yield by the use of NaOAc as base and DMSO-H\textsubscript{2}O (v/v= 10:1) mixture as solvent at 120 °C (62%, entry 3). It is worth mentioning that among all tested alloy compositions, rGO-CuPd catalyst provided the highest yield under the optimized conditions (Table 2, entries 12 and 13). Moreover, rGO-CuPd nanocatalyst provided a much higher yield than the commercially available Pd/C catalyst (entry 8) and comparable to that of the homogeneous catalyst. To the best of our knowledge, this is the first example of a comparison of the performance of a homogeneous and a heterogeneous catalyst in C-H arylation reactions.
With the optimized conditions in hand, we next investigated the scope of the fluoranthene synthesis reaction under both the homogeneous and heterogeneous catalytic conditions (Table 3). As aforementioned, fluoranthene product \(6b\) was obtained in 71 and 62\% yields using method A and B, respectively (entry 1). The reaction tolerates the presence of nitrile, amide and ketone groups, affording fluoranthene products \(7b\), \(8b\) and \(9b\) in good yields under both conditions (entries 2-4). While –CO\(_2\)Me
containing fluoranthene 10b was isolated in 78% yield with method A, method B gave a lower yield (36%, entry 5). 4- and 3-NO₂-substituted boronic acids 11a and 12a both gave the same fluoranthene product 11b in good yields (entries 6 and 7). The complete regioselectivity observed with substrate 12a is noteworthy to mention. Unsubstituted phenyl- and naphthyl-based boronic acids 13a and 14a are also competent substrates for the reaction under both homogeneous and heterogeneous catalytic conditions (entries 8 and 9). Gratifyingly, electron-rich 4-OMe-phenylboronic acid 15a afforded fluoranthene 15b in 74 and 63% yields with method A and B, respectively (entry 10). 3-CF₃-substituted boronic acid 16a reacts regioselectively to give product 16b under both conditions (entry 11). However, 3,5-bis(CF₃) substituted derivative 16a works only with method A (70% yield) whereas method B did not provide fluoranthene 17b (entry 12). In order to test a substrate with ortho-substitution, boronic acid 18a was examined, and fluoranthene 18b was obtained successfully (entry 13). Finally, in an attempt to synthesize a heteroatom-containing fluoranthene by our methodology, 4-pyridylboronic acid (19a) was tested, and we were pleased to obtain azafluoranthene 19b in 64 and 42% yields with method A and B, respectively (entry 14). This result underscores the potential of both catalytic conditions to be applied in the preparation of heteroaromatic fluoranthene analogues.
Table 3. Scope of the Fluoranthene Synthesis under both Homogeneous and Heterogeneous Catalytic Conditions$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>ArB(OR)$_2$</th>
<th>product</th>
<th>method</th>
<th>yield (%)</th>
<th>entry</th>
<th>ArB(OR)$_2$</th>
<th>product</th>
<th>method</th>
<th>yield (%)</th>
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<td></td>
<td></td>
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<td>A</td>
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<tr>
<td>1$^b$</td>
<td>(HO)$_2$B</td>
<td>6a</td>
<td></td>
<td>71</td>
<td>8$^c$</td>
<td>(HO)$_2$B</td>
<td>13a</td>
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<td>55</td>
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<td>F</td>
<td>6b</td>
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<td>F</td>
<td>13b</td>
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<td>7a</td>
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<tr>
<td>6$^b$</td>
<td>(HO)$_2$B</td>
<td>11a</td>
<td></td>
<td>72</td>
<td>13$^b$</td>
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<td>F</td>
<td></td>
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<tr>
<td></td>
<td>NO$_2$</td>
<td>11b</td>
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<td>NO$_2$</td>
<td>F</td>
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<td>7$^b$</td>
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<td>57</td>
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<td>N</td>
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$^a$Reaction conditions: Method A: 1.0 equiv of 5, 1.15 equiv of arylboronic acid or ester, 4.0 equiv of KOAc, 5 mol% of Pd(dppf)Cl$_2$, DMSO, 90 or 110 °C, N$_2$, 24 h. Method B: 1.0 equiv of 5, 1.15 equiv of arylboronic acid or ester, 5.0 equiv of NaOAc, 4.0 mg of rGO-CuPd nanocatalyst (1.8 mol% Pd loading), 120 °C, 24 h. $^b$T = 90 °C for Method A. $^c$T = 110 °C for Method A.
In order gain insight on the mechanism of the C-H arylation reaction, we conducted an intermolecular KIE experiment as a preliminary mechanistic study.\textsuperscript{14,15} For this purpose, we first prepared deuterated fluoranthene \textbf{13b-\textit{d}$^4$}, along with monoaryl/naphthalenes \textbf{20} and \textbf{20-\textit{d}$^5$} independently. When a 1:1 mixture of \textbf{20} and \textbf{20-\textit{d}$^5$} was treated with Pd(dppf)Cl\textsubscript{2} (5 mol\%) under the same reaction conditions but with a shorter reaction time (3 h), fluoranthene products \textbf{13b} and \textbf{13b-\textit{d}$^4$} were observed to be in a ratio of 1.1 by \textsuperscript{1}H-NMR spectroscopy (Scheme 1). Based on this result, it can be concluded that the C-H activation step is unlikely to be the rate-determining step in the overall intramolecular C-H arylation reaction.

\textbf{Scheme 1. Intermolecular KIE Experiment}

![Diagram of Scheme 1]

The reusability is one of the significant criteria for evaluating the performance of heterogeneous catalysts. Therefore, we tested the reusability of rGO-CuPd nanocatalysts in the synthesis of fluoranthene product \textbf{6b} (Table 3, entry 1). The nanocatalyst was found to be highly reusable affording the fluoranthene product \textbf{6b} in 62\%, 58\% and 55\% yields in three consecutive cycles (Figure 2a). It means that the rGO-CuPd nanocatalysts preserved almost 90\% of its initial catalytic activity after the third run. To get insight on the stability of rGO-CuPd, we analyzed the rGO-CuPd nanocatalysts by using TEM after the three-cycle reusability test. A representative TEM image given in Figure 2b reveals that no considerable change is observable on the overall dispersion and particle size of CuPd alloy NPs over rGO but there is a minimal deterioration on the morphology of CuPd NPs realized.
CONCLUSIONS

In summary, we have developed a new catalytic method that allows the synthesis of substituted fluoranthene derivatives via tandem Suzuki-Miyaura and intramolecular C-H arylation reactions. The reaction sequence was found to operate effectively under homogeneous catalytic conditions using Pd(dppf)Cl₂ as well as heterogeneous catalytic conditions using rGO-CuPd nanocatalysts. The reaction has a broad substrate scope and functional group tolerance, and fluoranthene products were obtained in good yields (up to 78%) when various arylboronic acids and esters having electron-withdrawing and donating groups with different substitution patterns were used. Moreover, rGO-CuPd nanocatalysts were found to be reusable heterogeneous catalysts in the presented method. A preliminary mechanistic study has also been conducted through an intermolecular KIE experiment. The reaction developed in this work represents a rare example of a transformation involving a C-H arylation step that can be promoted successfully under both homogeneous and heterogeneous catalytic conditions, and therefore, is expected to stimulate further research in this area.
EXPERIMENTAL SECTION

**General Information.** All reactions under homogeneous catalytic conditions were performed using oven-dried glassware under an inert atmosphere of nitrogen. Reactions were monitored by thin-layer chromatography (TLC) using aluminum-backed plates pre-coated with silica gel (60 Å, F254). UV light and KMnO₄ staining solution were used for TLC visualization. Flash column chromatography was performed on 200-400 mesh flash silica gel. NMR spectra were measured on a Bruker spectrometer at 400 MHz for ¹H-NMR spectra and 100 MHz for ¹³C spectra, and calibrated from internal standard (TMS, 0 ppm) or residual solvent signals (chloroform at 7.26 ppm, DMSO at 2.50 ppm for ¹H spectra; chloroform at 77.16 ppm and DMSO at 39.52 for ¹³C spectra). Infrared (FTIR) spectra were recorded on a Bruker Alpha-Platinum-ATR spectrometer with only selected peaks reported. HRMS data were obtained using a time-of-flight (TOF) mass spectrometer. Melting points are uncorrected.

1,8-Diiiodonaphthalene (5)¹⁶ and rGO-CuPd nanocatalysts¹²a were prepared according to reported procedures. All other commercially available reagents were used as received unless stated otherwise.

**General Procedure for Fluoranthene Synthesis Using Homogeneous Catalyst (Method A).** A 10-mL, oven-dried Schlenk tube was charged with 1,8-diiodonaphthalene (5) (100 mg, 0.26 mmol, 1.0 equiv) and DMSO (2 mL) under nitrogen atmosphere. Nitrogen gas was bubbled through the solution for 5 min with gentle stirring. Arylboronic acid or pinacol ester (0.30 mmol, 1.1 equiv), Pd(dppf)Cl₂•CH₂Cl₂ (11 mg, 0.013 mmol, 0.05 equiv) and KOAc (100 mg, 1.02 mmol, 4 equiv) were added sequentially to the solution. The Schlenk tube was then sealed with a glass stopper, and the reaction mixture was stirred at 90 °C or 110 °C for 24 h. The progress of the reaction was monitored by TLC. After cooling to ambient temperature, brine was added to the reaction mixture, and the aqueous phase was extracted with ethyl acetate (2 × 10 ml). The combined organic layer was dried over Na₂SO₄, filtered and concentrated *in vacuo*. The viscous crude product was purified by flash column
chromatography (silica gel) to afford the desired product.

**General Procedure for Fluoranethene Synthesis using Heterogeneous Catalyst (Method B).** A 10-mL Schlenk tube was charged with rGO-CuPd nanocatalyst (4.0 mg) and 2 mL of DMSO-H$_2$O mixture (DMSO:H$_2$O=10:1) under air. The suspension was sonicated for 30 min at room temperature. After complete dispersion of the catalyst to the solvent mixture, the Schlenk tube was fitted over a magnetic stirrer. 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol, 1.0 equiv), aryloboronic acid or pinacol ester (0.15 mmol, 1.1 equiv) and NaOAc • 3H$_2$O (54 mg, 0.65 mmol, 5 equiv) were added sequentially to the mixture with a gentle stirring. The Schlenk tube was then sealed with a glass stopper, and the reaction mixture was stirred at 120 °C for 24 h. The progress of the reaction was monitored by TLC. After cooling to ambient temperature, the reaction mixture was transferred to a centrifuge tube by washing with EtOAc. The mixture was centrifuged for 10 min under 6500 rpm. After complete precipitation of the catalyst, the organic layer was transferred to a separatory funnel and washed with brine. It was then dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. Purification by flash column chromatography (silica gel) gave the desired product.

**Procedure for the Recovery of the rGO-CuPd Catalyst.** After the completion of the reaction, the reaction mixture was transferred to a centrifuge tube by washing with EtOAc (8 mL). The mixture was centrifuged for 10 min, and the supernatant solution was decanted. The precipitated catalyst was washed additionally with EtOAc (8 mL), EtOH (2×8 mL) and acetone (8 mL). Centrifugation and decantation were repeated during each wash in order to remove any impurities and DMSO completely. The solid catalyst was dried at room temperature and used in the subsequent run for the reusability tests.

**8-Fluorofluoranethene (6b).** When 1,8-diiodonaphthalene (5) (100 mg, 0.26 mmol) was subjected to Method A at 90 °C, fluoranthene 6b was obtained as a white amorphous solid (41 mg, 71%) after purification by column chromatography (hexane only). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) gave 6b in 62% yield (18 mg). $R_f = 0.36$ (hexane); $^1$H NMR
Fluoranthene-8-carbonitrile (7b).

When 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) was subjected to Method A at 90 °C, fluoranthene 7b was obtained as an off-white solid (21 mg, 70%) after purification by column chromatography (hexane to EtOAc:hexane = 1:19). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) gave 7b in 68% yield (20.4 mg). R_f = 0.40 (EtOAc:hexane = 1:10); ^1H NMR (400 MHz, CDCl_3) δ 8.18 (1H, app s), 8.07 (1H, d, J = 6.9 Hz), 8.03 (1H, d, J = 7.0 Hz), 8.02–7.95 (3H, m), 7.74–7.68 (3H, m); ^13C NMR (100 MHz, CDCl_3) δ 143.2, 139.8, 135.1, 134.9, 132.7, 131.4, 130.1, 128.5, 128.4, 128.3, 128.0, 124.9, 122.0, 121.9, 121.4, 119.7, 110.5; FTIR (ATR, solid) 2921, 2223, 1736, 1454, 1422, 1259, 1187, 1019, 890, 812 cm\(^{-1}\); HRMS (APCI+) calcd for C_{17}H_{10}N [M+H]^+: 228.0808, found: 228.0809.

Fluoranthene-8-carboxamide (8b). When 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) was subjected to Method A at 90 °C, fluoranthene 8b was obtained as a pale yellow solid (21.7 mg, 67%) after purification by column chromatography (EtOAc:hexane = 1:1 to 4:1). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) gave 8b in 61% yield (19.6 mg). Mp. 227.4-228.9 °C; R_f = 0.21 (EtOAc:hexane = 3:1); ^1H NMR (400 MHz, DMSO-\(d^6\)) δ 8.58 (1H, dd, J = 1.6, 0.6 Hz), 8.22 (1H, d, J = 6.9 Hz), 8.19 (1H, d, J = 6.9 Hz), 8.14 (1H, dd, J = 7.9, 0.6 Hz), 8.09 (1H, br s), 8.04-8.00 (2H, m), 7.98 (1H, dd, J = 7.9, 1.6 Hz), 7.78-7.74 (2H, m), 7.45 (1H, br s); ^13C NMR (100 MHz, DMSO-\(d^6\)) δ 167.9, 141.1, 138.6, 135.6, 135.3, 133.6, 131.9, 129.6, 128.43, 128.37, 127.5, 127.23, 127.17, 121.7, 121.4, 121.1; FTIR (ATR, solid) 3410, 3189, 2923, 2852, 1649, 1610, 1435, 1387, 821,
1-(fluoranthen-8-yl)ethanone (9b).\(^{19}\) When 1,8-diiodonaphthalene (5) (100 mg, 0.26 mmol) was subjected to Method A at 90 °C, fluoranthene 9b was obtained as a white solid (31.6 mg, 49%) after purification by column chromatography (hexane to EtOAc:hexane = 1:19). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) gave 9b in 57% yield (18.5 mg). \(R_f = 0.31\) (EtOAc:hexane = 1:9); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.50 (1H, dd, \(J = 1.6, 0.7\) Hz), 8.03 (2H, d, \(J = 6.9\) Hz), 8.00-7.95 (2H, m), 7.91 (1H, d, \(J = 8.2\) Hz), 7.70-7.67 (2H, m), 2.71 (3H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 198.1, 143.8, 139.8, 136.5, 136.2, 135.9, 133.3, 130.2, 128.5, 128.4, 128.2, 128.1, 127.4, 121.6, 121.4, 120.9, 27.0; FTIR (ATR, solid) 2924, 1676, 1611, 1428, 1354, 1285, 1239, 816, 772 cm\(^{-1}\); HRMS (APCI+) calcd for C\(_{18}\)H\(_{13}\)O \([\text{M+H}]^+\): 245.0961, found: 245.0966.

Methyl fluoranthene-8-carboxylate (10b).\(^{20}\) When 1,8-diiodonaphthalene (5) (100 mg, 0.26 mmol) was subjected to Method A at 90 °C, fluoranthene 10b was obtained as a white solid (53.6 mg, 78%) after purification by column chromatography (EtOAc:hexane = 1:9). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) gave 10b in 36% yield (12.3 mg). \(R_f = 0.27\) (EtOAc:hexane = 1:9); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.5 (1H, dd, \(J = 1.5, 0.7\) Hz), 8.09 (1H, dd, \(J = 7.9, 1.6\) Hz), 8.00 (1H, d, \(J = 2.5\) Hz), 7.98 (1H, d, \(J = 2.5\) Hz), 7.93-7.86 (3H, m), 7.68-7.64 (2H, m), 3.99 (3H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 167.4, 143.6, 139.5, 136.2, 135.9, 131.5, 130.1, 129.3, 129.2, 128.3, 128.2, 127.9, 127.2, 122.8, 121.4, 121.2, 120.9, 52.3; FTIR (ATR, solid) 2949, 1716, 1436, 1290, 1245, 1118, 822, 773 cm\(^{-1}\); HRMS (APCI+) calcd for C\(_{18}\)H\(_{9}\)O \([\text{M+OMe}]^+\) 229.0648, found: 229.0714.

8-Nitrofluoranthene (11b).\(^{21}\) When 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) and 4-nitrophenylboronic acid (11a) (25 mg, 0.15 mmol) were subjected to Method A at 90 °C, fluoranthene 11b was obtained as a yellow solid (23.6 mg, 72%) after purification by column chromatography (EtOAc:hexane = 1:5). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol)
and 4-nitrophenylboronic acid (11a) (25 mg, 0.15 mmol) gave 11b in 70% yield (22.6 mg). The reactions between 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) and 3-nitrophenylboronic acid (12a) (25 mg, 0.15 mmol) gave fluoranthene 11b in 64% yield (21 mg) with Method A, and in 57% yield (18.6) with Method B. 

Rf = 0.32 (EtOAc:hexane = 1:4); 1H NMR (400 MHz, CDCl3) δ 8.61 (1H, d, J = 2.1 Hz), 8.21 (1H, dd, J = 8.3, 2.1 Hz), 8.01 (1H, d, J = 7.0 Hz), 7.97 (1H, d, J = 7.0 Hz), 7.96 (1H, d, J = 8.2 Hz), 7.93 (1H, d, J = 8.2 Hz), 7.89 (1H, d, J = 8.3 Hz), 7.71- 7.67 (2H, m); 13C NMR (100 MHz, CDCl3) δ 147.5, 144.9, 140.1, 134.9, 134.7, 133.5, 130.1, 128.8, 128.5, 128.4, 128.2, 123.1, 122.4, 121.7, 121.3, 116.8; FTIR (ATR, solid) 2924, 2851, 1517, 1487, 1452, 1338, 821, 772 cm⁻¹; HRMS (APCI-) calcd for C16H9NO2 [M]: 247.0639, found: 247.0598.

**Fluoranthe (13b).** When 1,8-diiodonaphthalene (5) (100 mg, 0.26 mmol) was subjected to Method A at 110 °C, fluoranthene 13b was obtained as a pale yellow solid (29 mg, 55%) after purification by column chromatography (hexane only). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) gave 13b in 56% yield (14.7 mg). Rf = 0.36 (hexane); 1H NMR (400 MHz, CDCl3) δ 7.97–7.92 (4H, m), 7.86 (2H, d, J = 8.3 Hz), 7.65 (2H, dd, J = 8.2, 6.9 Hz), 7.41-7.39 (2H, m); 13C NMR (100 MHz, CDCl3) δ 139.6, 137.1, 130.22, 130.15, 128.1, 128.5, 128.4, 128.2, 123.1, 122.4, 121.7, 120.2; FTIR (ATR, solid) 3051, 2924, 1454, 1439, 826, 774, 747 cm⁻¹; GCMS (m/z) 202.2.

**Benzo[j]fluoranthe (14b).** When 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) was subjected to Method A at 110 °C, fluoranthene 14b was obtained as a pale yellow solid (20.6 mg, 62%) after purification by column chromatography (hexane only). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) gave 14b in 59% yield (19.6 mg). Rf = 0.33 (hexane); 1H NMR (400 MHz, CDCl3) δ: 8.72 (1H, d, J = 8.5 Hz), 8.46 (1H, d, J = 7.0 Hz), 8.06 (1H, d, J = 8.3 Hz), 8.01 (1H, d, J = 6.9 Hz), 7.95-7.92 (1H, m), 7.88–7.86 (2H, m), 7.72–7.60 (3H, m), 7.49 (1H, ddd, J = 8.1, 6.8, 1.1 Hz); 13C NMR (100 MHz, CDCl3) δ: 138.0, 137.9, 137.3, 134.4, 134.2, 132.1, 130.8, 129.8, 129.5, 128.5, 128.3, 128.0, 127.5, 127.12, 127.07, 125.4, 124.4, 124.3, 121.0, 120.0.
8-Methoxyfluoranthene (15b). When 1,8-diiiodonaphthalene (5) (50 mg, 0.13 mmol) was subjected to Method A at 110 °C, fluoranthene 15b was obtained as a yellow solid (22.6 mg, 74%) after purification by column chromatography (hexane to EtOAc/hexane = 1/9). Application of Method B using 1,8-diiiodonaphthalene (5) (50 mg, 0.13 mmol) gave 15b in 63% yield (19.4 mg). Rf = 0.30 (EtOAc:hexane = 1:9); 1H NMR (400 MHz, CDCl3) δ 7.91 (1H, d, J = 6.9 Hz), 7.85-7.76 (4H, m), 7.64-7.58 (2H, m), 7.47 (1H, d, J = 2.4 Hz), 6.92 (1H, dd, J = 8.3, 2.4 Hz), 3.94 (3H, s); 13C NMR (100 MHz, CDCl3) δ 160.2, 141.4, 137.2, 137.0, 133.1, 132.6, 130.1, 128.2, 127.9, 127.1, 125.6, 122.4, 120.1, 119.1, 113.0, 107.9, 55.8; FTIR (ATR, solid) 2920, 2849, 1603, 1455, 1416, 1221, 1173, 1025 cm⁻¹; HRMS (APCI+) calcd for C17H13O [M+H]+: 233.0961, found: 233.0963.

8-(Trifluoromethyl)fluoranthene (16b). When 1,8-diiiodonaphthalene (5) (100 mg, 0.26 mmol) was subjected to Method A at 90 °C, fluoranthene 16b was obtained as a white solid (37 mg, 52%) after purification by column chromatography (hexane only). Application of Method B using 1,8-diiiodonaphthalene (5) (50 mg, 0.13 mmol) gave 16b in 58% yield (20.6 mg). Rf = 0.32 (hexane); 1H NMR (400 MHz, CDCl3) δ 8.11 - 8.10 (1H, m), 7.97-7.88 (5H, m), 7.67-7.62 (3H, m); 13C NMR (100 MHz, CDCl3) δ 142.5, 139.8, 135.7, 135.6, 132.9, 130.1, 129.5 (q, J_C-F = 32.0 Hz), 128.3, 128.2, 127.9, 127.6, 124.6 (q, J_C-F = 3.9 Hz), 121.5, 121.4, 121.0, 118.4 (q, J_C-F = 3.9 Hz); 19F NMR (376 MHz, CDCl3) δ -61.9; FTIR (ATR, solid) 1458, 1431, 1325, 1262, 1157, 1113 cm⁻¹; GCMS (m/z) 270.1.

7,9-Bis(trifluoromethyl)fluoranthene (17b). When 1,8-diiiodonaphthalene (5) (100 mg, 0.26 mmol) was subjected to Method A at 110 °C, fluoranthene 17b was obtained as a white solid (31 mg, 70%) after purification by column chromatography (hexane only). Mp. 138.9-140.7 °C; Rf = 0.32 (hexane); 1H NMR (400 MHz, CDCl3) δ 8.36 (1H, d, J = 7.2 Hz), 8.30 (1H, s), 8.05 (1H, d, J = 7.0 Hz), 8.01 (1H, d, J = 8.2 Hz), 7.98 (1H, d, J = 8.2 Hz), 7.93 (1H, s), 7.77-7.69 (2H, m); 13C NMR (100 MHz, CDCl3) δ 141.9, 134.0, 132.9, 132.6, 130.1, 129.3, 128.8, 128.1, 126.6 (q, J_C-F = 4.9 Hz), 125.4, 122.7, 121.7-121.5 (m), 121.3-121.2 (m); 19F NMR (376 MHz, CDCl3) δ - 62.2, -63.0; FTIR (ATR, solid)
1583, 1444, 1357, 1299, 1277, 1161, 1119 cm\(^{-1}\); HRMS (APCI-) calcd for C\(_{18}\)H\(_8\)F\(_6\) [M]\(^+\) 338.0536, found: 338.0532.

7-Fluorofluoranthene (18b).\(^{17}\) When 1,8-diiodonaphthalene (5) (100 mg, 0.26 mmol) was subjected to Method A at 90 °C, fluoranthene 18b was obtained as a white amorphous solid (37.9 mg, 65%) after purification by column chromatography (hexane only). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) gave 18b in 46% yield (13.4 mg). \(R_f = 0.36\) (hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (1H, d, \(J = 6.9\) Hz), 7.95 (1H, d, \(J = 6.9\) Hz), 7.88 (1H, d, \(J = 8.2\) Hz), 7.87 (1H, d, \(J = 8.2\) Hz), 7.71-7.63 (3H, m), 7.34 (1H, ddd, \(J = 8.2, 7.5, 5.1\) Hz), 7.11 (1H, ddd, \(J = 9.7, 8.3, 0.7\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.3 (d, \(J_{C-F} = 250.2\) Hz), 142.3 (d, \(J_{C-F} = 6.4\) Hz), 136.5 (d, \(J_{C-F} = 2.1\) Hz), 134.0 (d, \(J_{C-F} = 1.6\) Hz), 132.1, 130.1, 129.1 (d, \(J_{C-F} = 7.3\) Hz), 128.4, 128.0, 127.4, 126.9, 125.8 (d, \(J_{C-F} = 16.1\) Hz), 123.7 (d, \(J_{C-F} = 4.0\) Hz), 121.0, 117.6 (d, \(J_{C-F} = 2.9\) Hz), 114.9 (d, \(J_{C-F} = 20.2\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -118.3; FTIR (ATR, solid) 3045, 1572, 1445, 1236, 1178, 823, 794, 769 cm\(^{-1}\); GCMS (m/z) 220.1.

Acenaphtho[1,2-c]pyridine (19b). When 1,8-diiodonaphthalene (5) (100 mg, 0.26 mmol) was subjected to Method A at 110 °C, azafluoranthene 19b was obtained as a pale green sticky solid (34.7 mg, 64%) after purification by column chromatography (EtOAc:hexane = 1:1 to 4:1). Application of Method B using 1,8-diiodonaphthalene (5) (50 mg, 0.13 mmol) gave 19b in 42% yield (11.4 mg). \(R_f = 0.18\) (EtOAc:hexane = 2:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.16 (1H, s), 8.64 (1H, d, \(J = 5.0\) Hz), 8.03 (1H, d, \(J = 7.0\) Hz), 8.01 (1H, d, \(J = 6.9\) Hz), 7.97 (1H, d, \(J = 8.2\) Hz), 7.89 (1H, d, \(J = 8.2\) Hz), 7.78 (1H, dd, \(J = 5.0, 1.1\) Hz), 7.70-7.64 (2H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.8, 146.3, 143.0, 134.70, 134.69, 134.3, 132.4, 130.2, 129.2, 128.4, 128.1, 127.5, 122.6, 121.5, 116.5; FTIR (ATR, solid) 3010, 3000, 1633, 1600, 1454, 1422, 1187, 820, 773 cm\(^{-1}\); HRMS (ESI+) calcd for C\(_{15}\)H\(_{10}\)N [M+H]\(^+\): 204.0808, found: 204.0816.

1-Iodo-8-phenylnaphthalene (20).\(^{22}\) A 10-mL, oven-dried Schlenk tube was charged with 1,8-
diiodonaphthalene (5) (100 mg, 0.26 mmol, 1.0 equiv) and DMF (2 mL) under nitrogen atmosphere. Nitrogen gas was bubbled through the solution for 5 min with gentle stirring. Phenylboronic acid (13a) (41 mg, 0.33 mmol, 1.3 equiv), Pd(PPh₃)₄ (15 mg, 0.013 mmol, 0.05 equiv.), K₂CO₃ (140 mg, 1.0 mmol, 4 equiv) were added sequentially to the solution. The reaction mixture was stirred at 80 °C for 24 h. The progress of the reaction was monitored by TLC. After cooling to ambient temperature, brine was added to the reaction mixture, and the aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic layer was dried over Na₂SO₄, filtered and concentrated in vacuo. The viscous crude product was purified by flash column chromatography (hexane only) to afford product 20 (31 mg, 36%) as a colorless oil. Rᵣ = 0.38 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.22 (1H, dd, J = 7.3, 1.3 Hz), 7.92 (1H, dd, J = 8.1, 1.2 Hz), 7.86 (1H, dd, J = 7.3, 2.2 Hz), 7.53–7.42 (5H, m), 7.35-7.33 (2H, m), 7.11 (1H, t, J = 7.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 141.7, 141.5, 135.7, 131.6, 131.24, 131.15, 129.9, 129.2, 127.9, 127.5, 126.7, 125.3, 92.2; GCMS (m/z) 330.0.

20-d₅. Compound 20-d₅ was synthesized via the same procedure used for compound 20 starting from 1,8-diiodonaphthalene (5) and the commercially available phenyl-d₅-boronic acid. The crude reaction mixture was purified by flash column chromatography (hexane only) to afford product 20-d₅ (25 mg, 28%) as a colourless oil. Rᵣ = 0.38 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.23 (1H, dd, J = 7.3, 1.0 Hz), 7.92 (1H, d, J = 8.1 Hz), 7.87 (1H, dd, J = 7.3, 2.2 Hz), 7.53-7.48 (2H, m), 7.11 (1H, t, J = 7.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 141.7, 141.3, 135.7, 131.2, 129.9, 129.2, 126.7, 125.3, 92.2; GCMS (m/z) 335.1.

Fluoranthene-d₄ (13b-d₄): Rᵣ = 0.36 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.95 (2H, dd, J = 7.0, 0.5 Hz), 7.85 (2H, dd, J = 8.3, 0.6 Hz), 7.64 (2H, dd, J = 8.2, 6.9 Hz); GCMS (m/z) 206.2.

**Intermolecular Kinetic Isotope Effect Study.** A 10-mL, oven-dried Schlenk tube was charged with 20 (20 mg, 0.06 mmol) and 20-d₅ (20 mg, 0.06 mmol) followed by addition of DMSO (2 mL) under nitrogen atmosphere. Nitrogen gas was bubbled through the solution for 5 min with gentle
stirring. Pd(dppf)Cl$_2$•CH$_2$Cl$_2$ (5 mg, 0.006 mmol) and KOAc (0.5 mmol) were added sequentially to the reaction mixture. The Schlenk tube was then sealed with a glass stopper, and the reaction mixture was stirred at 90 °C for 3 h. After cooling to ambient temperature, brine was added to the reaction mixture, and the aqueous phase was extracted with ethyl acetate (2 × 10 ml). The combined organic layer was dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude reaction mixture was purified by flash column chromatography (hexane only) to afford a mixture of product 13b and 13b-$d_4$ (7.3 mg, 30%) as a viscous oil. The ratio of the two products was determined by $^1$H-NMR spectroscopy where the intermolecular kinetic isotopic effect (KIE) $k$(H)/$k$(D) was found to be 1.1 based on integration analysis. This experiment was repeated twice, and the same result was obtained in both experiments.

ASSOCIATED CONTENT
The Supporting Information is available free of charge on the ACS Publications website. TEM and XRD images, and NMR spectra (PDF).

AUTHOR INFORMATION
Corresponding Authors
*E-mail: yeturkmen@bilkent.edu.tr
*E-mail: ometin@atauni.edu.tr

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(13) See the Supporting Information for the detailed structural characterization of CuPD alloy NPs and rGO-CuPd nanocatalysts by TEM and XRD.


Homogeneous Pd catalyst or
Heterogeneous rGO-CuPd nanocatalyst

- 14 examples
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