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

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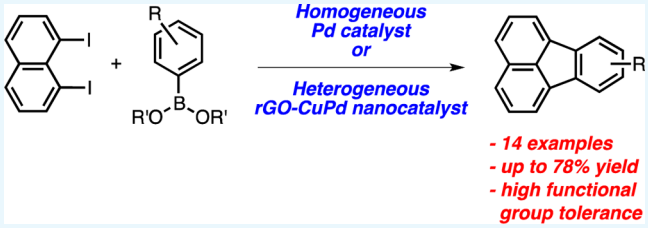
Supporting Information

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 $Pd(dppf)Cl_2$ as well as heterogeneous catalysis using reduced graphene oxide (rGO)-CuPd nanocatalysts with low catalyst loadings. High functional group tolerance is observed under both catalytic conditions where arylboronic acids and esters having electron-withdrawing and electron-donating substituents afforded fluoranthene products in good yields (up to 78%). Moreover, the 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 with a broad range of attractive applications.[1] A number of fungal natural products have a 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, Hartl, Li, and co-workers, and their field-effect mobilities have been investigated (Figure 1).[5]

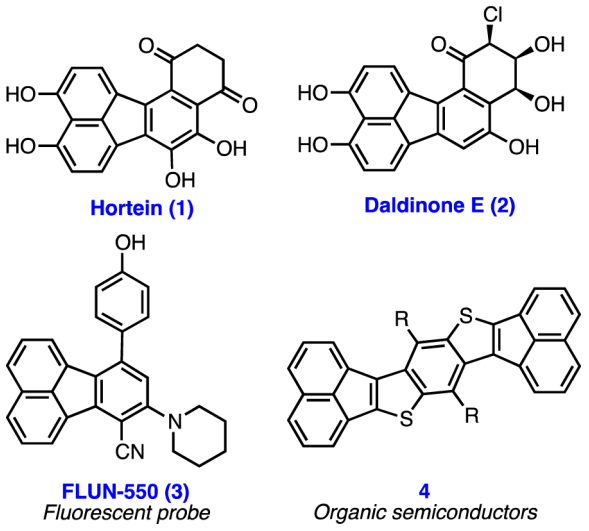


Figure 1. Examples of important fluoranthene analogues.

Among the methods available for the synthesis and derivatization of fluoranthenes, Diels−Alder reaction has been the most commonly utilized method,[3a−c,4,6] whereas transition-metal-catalyzed reactions and various other cyclization strategies have also been employed.[3d,5,7] In 2009, Quimby and Scott 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.[8] 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.[9] More recently, Manabe and co-workers developed an elegant Pd-catalyzed method that enables the three-step synthesis of fluoranthenes via inter- and intramolecular C−H arylation reactions.[10] 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

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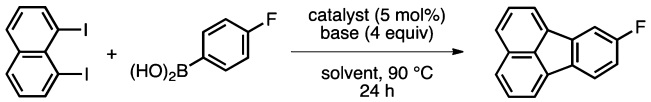
reaction using a tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$) catalyst starting from 1,8-diiodonaphthalene (**5**). On the other hand, using a more active Pd catalyst, $Pd(dppf)Cl_2$ led to the formation of significant amounts of fluoranthene side products, which prompted us to investigate 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-diiodonaphthalene (**5**) and 4-fluorophenylboronic acid (**6a**) in the presence of homogeneous Pd catalysts (Table 1). As

Table 1. Optimization Studies Using Homogeneous Catalysts[a]



5 **6a** **6b**

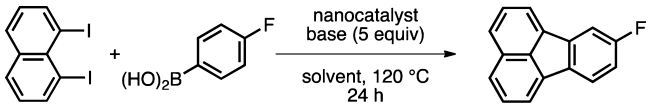
entry	catalyst	base	solvent	yield (%)[b]
1	$Pd(PPh_3)_4$	KOAc	DMSO	<5
2	$Pd(dppf)Cl_2$	K_2CO_3	DMSO	10
3	$Pd(dppf)Cl_2$	Cs_2CO_3	DMSO	35
4	$Pd(dppf)Cl_2$	Na_2CO_3	DMSO	28
5	$Pd(dppf)Cl_2$	KOAc	DMSO	71
6	$Pd(dppf)Cl_2$	NaOAc	DMSO	69
7	$Pd(dppf)Cl_2$	KO^{t}Bu	DMSO	<5
8	$Pd(dppf)Cl_2$	CsF	DMSO	37
9	$Pd(dppf)Cl_2$	NaOH	DMSO	<5
10	$Pd(dppf)Cl_2$	KOAc	DMF	<5
11[c]	$Pd(dppf)Cl_2$	KOAc	CH_3CN	31
12	$Pd(dppf)Cl_2$	KOAc	dioxane	48
13	$Pd(dppf)Cl_2$	KOAc	DMA	38
14[d]	$Pd(OAc)_2/P^tBu_3{\cdot}HBF_4$	KOAc	DMSO	21
15[e]	$Pd_2(dba)_3/P^tBu_3{\cdot}HBF_4$	KOAc	DMSO	14

[a]0.13 mmol **5**, 0.15 mmol **6a**, 0.52 mmol base, 5 mol % of Pd catalyst, 90 °C, N_2, 24 h. [b]Isolated yields. [c]T = 80 °C. [d]$P^tBu_3{\cdot}HBF_4/Pd(OAc)_2$ = 2:1. [e]$P^tBu_3{\cdot}HBF_4/Pd_2(dba)_3$ = 4:1. Abbreviations: dppf, 1,1′-bis(diphenylphosphino)ferrocene and dba, dibenzylideneacetone.

mentioned above, 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 dimethyl sulfoxide (DMSO) at 90 °C (71%, entries 2−6). Inferior results were obtained when KO^{t}Bu, CsF, and NaOH were examined as bases (entries 7−9). With KOAc as the optimal base, we then performed a solvent screening. Whereas dimethylformamide (DMF) was completely ineffective under the same reaction conditions (entry 10), CH_3CN, dioxane, and *N*,*N*-dimethylacetamide (DMA) afforded the desired product **6b**, albeit in lower yields (31, 48, and 38%, respectively, entries 11−13). Finally, $Pd(OAc)_2/P^tBu_3{\cdot}HBF_4$ and $Pd_2(dba)_3/P^tBu_3{\cdot}HBF_4$ combinations were found be catalytically less active compared to $Pd(dppf)Cl_2$ (entries 14 and 15).

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 homogeneous 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.[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;[12] especially, rGO-assembled CuPd alloy NPs (rGO-CuPd) were shown to be highly efficient heterogeneous catalysts in Sonogashira cross-coupling reactions.[12a] By the motivation of these promising results, we selected the rGO-CuPd nanocatalyst as a heterogeneous catalyst to be tested in this transformation.[13] We first conducted optimization experiments depending on various parameters in the presence of the rGO-CuPd nanocatalyst (Table 2). As can be seen in Table 2,

Table 2. Optimization Studies Using Heterogeneous NP Catalysts[a]



5 **6a** **6b**

entry	catalyst	base	solvent	yield (%)[b]
1	rGO-CuPd	NaOAc	DMSO	46
2	rGO-CuPd	NaOAc	DMSO/H_2O[c]	37
3	rGO-CuPd	NaOAc	DMSO/H_2O[d]	62
4[e]	rGO-CuPd	NaOAc	DMSO/H_2O[d]	51
5[f]	rGO-CuPd	NaOAc	DMSO/H_2O[d]	44
6	rGO-CuPd	NaOAc	DMF/H_2O[g]	<5
7	rGO-CuPd	NaOAc	DMA/H_2O[h]	55
8	Pd/C[i]	NaOAc	DMSO/H_2O[d]	26
9	rGO-CuPd	KOAc	DMSO/H_2O[d]	43
10	rGO-CuPd	K_2CO_3	DMSO/H_2O[d]	32
11	rGO-CuPd	Cs_2CO_3	DMSO/H_2O[d]	21
12	rGO-$Cu_{32}Pd_{68}$	NaOAc	DMSO/H_2O[d]	19
13[j]	rGO-$Cu_{75}Pd_{25}$	NaOAc	DMSO/H_2O[d]	<5

[a]Reaction conditions: 0.13 mmol **5**, 0.15 mmol **6a**, 0.65 mmol base, 4.0 mg of nanocatalyst (rGO-CuPd contains 6.5 wt % Pd corresponding to 0.0024 mmol Pd and 1.8 mol % Pd loading), 120 °C, 24 h. [b]Isolated yields. [c]DMSO/H_2O = 5:1. [d]DMSO/H_2O = 10:1. [e]2.0 mg of nanocatalyst was used. [f]T = 100 °C. [g]DMF/H_2O = 10:1. [h]DMA/H_2O = 10:1. [i]10 wt % Pd on carbon (5.0 mg). [j]5.0 mg of catalyst was used.

the rGO-CuPd nanocatalyst provided the highest yield by the use of NaOAc as a base and DMSO/H_2O (v/v = 10:1) mixture as a solvent at 120 °C (62%, entry 3). It is worth mentioning that among all tested alloy compositions, the rGO-CuPd catalyst provided the highest yield under the optimized conditions (Table 2, entries 12 and 13). Moreover, the 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 performances of a homogeneous and a heterogeneous catalyst in C−H arylation reactions.

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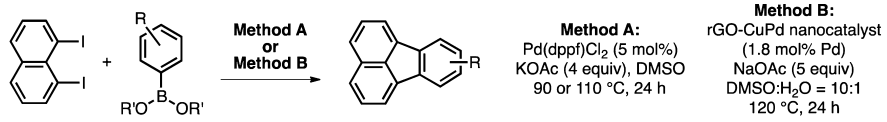
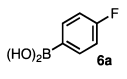
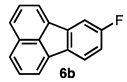
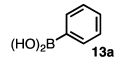
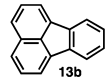
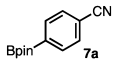
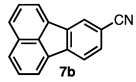
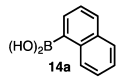
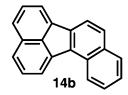
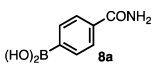
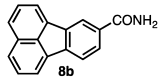
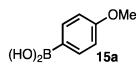
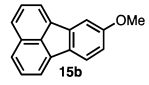
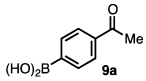
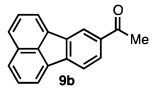
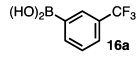
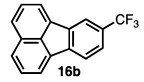
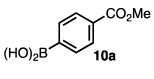
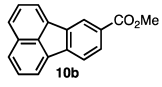
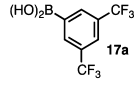
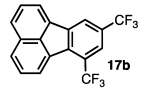
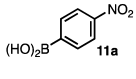
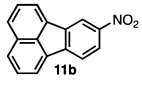
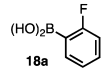
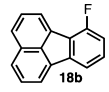
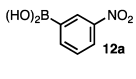
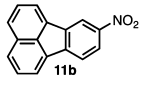
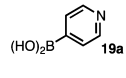
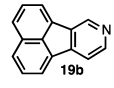
Table 3. Scope of the Fluoranthene Synthesis under Both Homogeneous and Heterogeneous Catalytic Conditions[a]



entry	$ArB(OR)_2$	product	yield (%) method A	yield (%) method B	entry	$ArB(OR)_2$	product	yield (%) method A	yield (%) method B
1[b]	 **6a**	 **6b**	71	62	8[c]	 **13a**	 **13b**	55	56
2[b]	 **7a**	 **7b**	70	68	9[c]	 **14a**	 **14b**	62	59
3[b]	 **8a**	 **8b**	67	61	10[c]	 **15a**	 **15b**	74	63
4[b]	 **9a**	 **9b**	49	57	11[b]	 **16a**	 **16b**	52	58
5[b]	 **10a**	 **10b**	78	36	12[c]	 **17a**	 **17b**	70	<5
6[b]	 **11a**	 **11b**	72	70	13[b]	 **18a**	 **18b**	65	46
7[b]	 **12a**	 **11b**	64	57	14[c]	 **19a**	 **19b**	64	42

[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.

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 mentioned above, fluoranthene product **6b** was obtained in 71 and 62% yields using methods 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). Whereas $-CO_2Me$-containing fluoranthene **10b** was isolated in 78% yield with method A, method B gave a lower yield (36%, entry 5). 4- and 3-NO_2-substituted boronic acids **11a** and **12a** both gave the same fluoranthene product **11b** in good yields (entries 6 and 7, respectively). 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, respectively). Gratifyingly, electron-rich 4-OMe-phenylboronic acid **15a** afforded fluoranthene **15b** in 74 and 63% yields with methods A and B, respectively (entry 10). 3-CF_3-substituted boronic acid **16a** reacts regioselectively to give product **16b** under both conditions (entry 11). However, 3,5-bis(CF_3)-substituted derivative **16a** works only with method A (70% yield), whereas method B did not provide fluoranthene **17b** (entry 12). 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 methods 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.

To gain insights into the mechanism of the C−H arylation reaction, we conducted an intermolecular kinetic isotope effect (KIE) experiment as a preliminary mechanistic study.[14,15] For this purpose, we first prepared deuterated fluoranthene **13b**-d_4 along with monoarylnaphthalenes **20** and **20**-d_5 independently. When a 1:1 mixture of **20** and **20**-d_5 was treated with $Pd(dppf)Cl_2$ (5 mol %) under the same reaction conditions but with a shorter reaction time (3 h), fluoranthene products **13b** and **13b**-d_4 were observed to be in a ratio of 1.1 by ^{1}H NMR spectroscopy (Scheme 1). On the basis of this result, it can be

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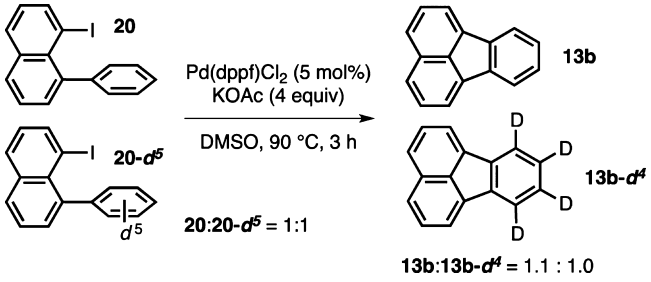
concluded that the C−H activation step is unlikely to be the rate-determining step in the overall intramolecular C−H arylation reaction.

Scheme 1. Intermolecular KIE Experiment



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 **6b** (Table 3, entry 1). The nanocatalysts were found to be highly reusable, affording the fluoranthene product **6b** in 62, 58, and 55% yields in three consecutive cycles (Figure 2a). This means that the rGO-CuPd nanocatalysts preserved almost 90% of their initial catalytic activity after the third run. To get insights into the stability of the rGO-CuPd, we analyzed the rGO-CuPd nanocatalysts by using transmission electron microscopy (TEM) after the three-cycle reusability test. A representative TEM image given in Figure 2b reveals that no considerable change is observable in the overall dispersion and particle size of the CuPd alloy NPs over rGO but there is a minimal deterioration on the morphology of the 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 $Pd(dppf)Cl_2$ 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 electron-donating groups with different substitution patterns were used. Moreover, the 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 precoated with silica gel (60 Å, F_{254}). UV light and $KMnO_4$ 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 at 100 MHz for ^{13}C 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 and chloroform at 77.16 ppm and DMSO at 39.52 for ^{13}C spectra). Infrared [Fourier transform infrared (FTIR)] spectra were recorded on a Bruker Alpha-Platinum-ATR spectrometer, with only selected peaks reported. High-resolution mass spectrometry (HRMS) data were obtained using a time-of-flight mass spectrometer. Melting points are uncorrected.

1,8-Diiodonaphthalene (**5**)[16] and rGO-CuPd nanocatalysts[12a] 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 Catalysts (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 a 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), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (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 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

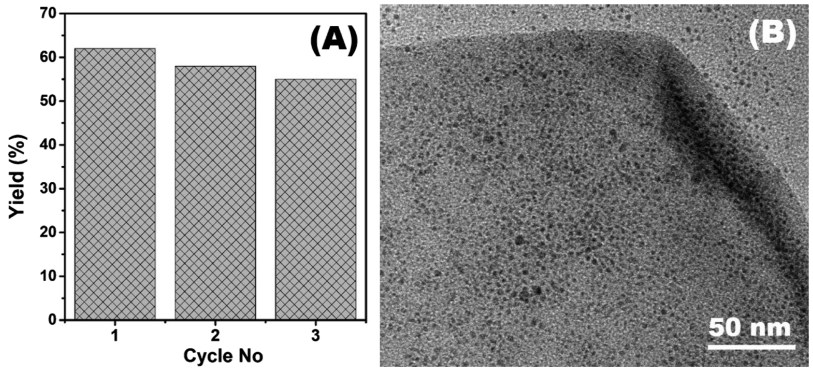


Figure 2. (A) Three-cycle reusability test for the rGO-CuPd nanocatalysts in the fluoranthene synthesis. (B) Representative TEM image of the rGO-CuPd nanocatalysts after the three-cycle reusability test.

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aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic layer was dried over Na_2SO_4, 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 Fluoranthene Synthesis Using Heterogeneous Catalysts (Method B). A 10 mL Schlenk tube was charged with the rGO-CuPd nanocatalyst (4.0 mg) and 2 mL of DMSO/H_2O mixture (DMSO/H_2O = 10:1) under air. The suspension was sonicated for 30 min at room temperature. After complete dispersion of the catalyst in the solvent mixture, the Schlenk tube was fitted over a magnetic stirrer. 1,8-Diiodonaphthalene (**5**) (50 mg, 0.13 mmol, 1.0 equiv), arylboronic acid or pinacol ester (0.15 mmol, 1.1 equiv), and NaOAc·3H_2O (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_2SO_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 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-Fluorofluoranthene (6b).[17] 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 (400 MHz, $CDCl_3$): δ 7.92−7.81 (5H, m), 7.66−7.61 (2H, m), 7.58 (1H, dd, J = 8.8, 2.4 Hz), 7.08 (1H, ddd, J = 9.2, 8.3, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2 (d, J_{C-F} = 245.1 Hz), 141.7 (d, J_{C-F} = 9.1 Hz), 136.3 (d, J_{C-F} = 0.6 Hz), 136.2 (d, J_{C-F} = 2.9 Hz), 135.5 (d, J_{C-F} = 2.6 Hz), 133.0 (d, J_{C-F} = 1.2 Hz), 130.1, 128.2, 128.1, 127.5, 126.4 (d, J_{C-F} = 1.0 Hz), 122.5 (d, J_{C-F} = 9.2 Hz), 120.7, 120.0 (d, J_{C-F} = 1.4 Hz), 114.2 (d, J_{C-F} = 23.4 Hz), 109.2 (d, J_{C-F} = 22.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −114.5; FTIR (ATR, solid): 3045, 1580, 1452, 1263, 1172, 1130, 870, 813, 768 cm^{-1}; GCMS (m/z): 220.1.

Fluoranthene-8-carbonitrile (7b).[18] 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); ^{1}H 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); ^{13}C 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); ^{1}H 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); ^{13}C 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, 770 cm^{-1}; HRMS (APCI$^+$): calcd for $C_{17}H_{12}NO$ [M + H]$^+$, 246.0913; found, 246.0935.

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, $CDCl_3$): δ 8.50 (1H, dd, J = 1.6, 0.7 Hz), 8.03 (2H, d, J = 6.9 Hz), 8.00−7.95 (2H, m), 7.93 (1H, d, J = 8.2 Hz), 7.90 (1H, d, J = 8.2 Hz), 7.70−7.67 (2H, m), 2.71 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 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 $C_{18}H_{13}O$ [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, $CDCl_3$): δ 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, $CDCl_3$): δ 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 $C_{17}H_9O$ [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

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(**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. R_f = 0.32 (EtOAc/hexane = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{16}H_9NO_2$ [M]$^-$, 247.0639; found, 247.0598.

Fluoranthene (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). R_f = 0.36 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 137.1, 130.22, 130.15, 128.1, 127.7, 126.8, 121.7, 120.2; FTIR (ATR, solid): 3051, 2924, 1454, 1439, 826, 774, 747 cm^{-1}; GCMS (m/z), 202.2.

Benzo[*j*]fluoranthene (14b).[7a] 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). R_f = 0.33 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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).[10] When 1,8-diiodonaphthalene (**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-diiodonaphthalene (**5**) (50 mg, 0.13 mmol) gave **15b** in 63% yield (19.4 mg). R_f = 0.30 (EtOAc/hexane = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{17}H_{13}O$ [M + H]$^+$, 233.0961; found, 233.0963.

8-(Trifluoromethyl)fluoranthene (16b).[10] When 1,8-diiodonaphthalene (**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-diiodonaphthalene (**5**) (50 mg, 0.13 mmol) gave **16b** in 58% yield (20.6 mg). R_f = 0.32 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11−8.10 (1H, m), 7.97−7.88 (5H, m), 7.67−7.62 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$): 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); ^{19}F NMR (376 MHz; $CDCl_3$): 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-diiodonaphthalene (**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; R_f = 0.32 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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); ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.2, −63.0; FTIR (ATR, solid): 1583, 1444, 1357, 1299, 1277, 1161, 1119 cm^{-1}; HRMS (APCI$^-$): calcd for $C_{18}H_8F_6$ [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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ −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, $CDCl_3$): δ 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, $CDCl_3$): δ 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 a 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), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol, 0.05 equiv), and K_2CO_3 (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

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was extracted with ethyl acetate (2 × 10 mL). The combined organic layer was dried over Na_2SO_4, 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. R_f = 0.38 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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-d_5. Compound **20-d_5** was synthesized via the same procedure used for compound **20** starting from 1,8-diiodonaphthalene (**5**) and the commercially available phenyl-d_5-boronic acid. The crude reaction mixture was purified by flash column chromatography (hexane only) to afford the product **20-d_5** (25 mg, 28%) as a colorless oil. R_f = 0.38 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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-d_4 (13b-d_4). R_f = 0.36 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): 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 KIE Study. A 10 mL oven-dried Schlenk tube was charged with **20** (20 mg, 0.06 mmol) and **20-d_5** (20 mg, 0.06 mmol), followed by the addition of DMSO (2 mL) under a nitrogen atmosphere. Nitrogen gas was bubbled through the solution for 5 min with gentle stirring. Pd(dppf)-Cl_2·CH_2Cl_2 (5 mg, 0.006 mmol) and KOAc (50 mg, 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_2SO_4, filtered, and concentrated in vacuo. The crude reaction mixture was purified by flash column chromatography (hexane only) to afford a mixture of the products **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 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

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01566.

TEM and X-ray diffraction images and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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