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A Three-Step Process To Facilitate the Annulation of Polycyclic Aromatic Hydrocarbons

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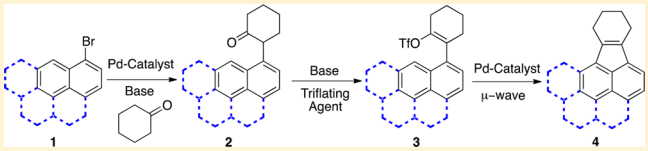
Supporting Information

ABSTRACT: A new efficient three-step process to annulate polycyclic aromatic hydrocarbons (PAHs) has been developed, providing access to PAHs with saturated rings that under current chemical methods would be difficult to produce in an efficient manner. This method relies on a palladium-catalyzed cross-coupling reaction of various brominated PAHs with cyclohexanone to yield α-arylated ketones, which are converted to regiospecific vinyl triflates and cyclized by a palladium-catalyzed intramolecular arene−vinyl triflate coupling to produce PAHs with incorporated saturated rings or "tetrahydroindeno-annulated" PAHs.



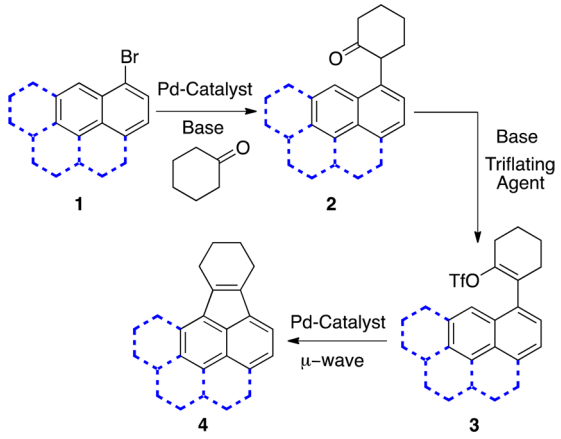
INTRODUCTION

In recent years, the synthesis of complex polycyclic aromatic hydrocarbons (PAHs), such as large flat PAHs,[1] saddle-shaped PAHs,[2] belt-shaped species,[3] geodesic polyarenes,[4,5] and single-walled carbon nanotubes (SWCNTs),[6] has become vitally important to the development of organic materials[7] because of their physical and electronic properties. As the interest in these non-natural products has increased, the number of synthetic methods that can be employed to create these molecules has not kept pace.

The key step in the chemical synthesis of complex PAHs, specifically geodesic polyarenes, is an annulation reaction that forms five-membered rings. Currently, there are three main methods to create five-membered rings within PAHs; these are flash vacuum pyrolysis (FVP),[8] acid-catalyzed cyclodehydration,[9] and palladium-catalyzed cyclization.[10,11] In recent years palladium-catalyzed cyclization has become the preferred method for PAH synthesis. This method was pioneered in the early 1990s by Rice and co-workers[10] with the development of an ingenious multistep process to create a vast array of PAHs. Their process relies upon an intramolecular palladium-catalyzed arene−triflate coupling reaction to produce their desired PAH products. This arene−triflate coupling reaction is an efficient process; however, the production of the synthetic intermediates for this process requires harsh reaction conditions and multiple functional group transformations and cannot be used to create PAHs with saturated rings.

In this paper, we present a new process to efficiently annulate PAHs that utilizes mild reaction conditions and minimal functional group transformations to produce a wide variety of PAHs that contain saturated rings. Our new method relies on a palladium-catalyzed cross-coupling reaction of a brominated PAH (**1**) with cyclohexanone to produce an α-arylated ketone (**2**),[12] which can be converted to a vinyl triflate (**3**). This conversion is followed by a palladium-catalyzed intramolecular arene−vinyl triflate coupling[10,13] to close a five-membered ring, producing a tetrahydroindeno-annulated PAH (**4**) that is highly soluble in various organic solvents (Scheme 1). An extension of our process to multiple annulations could allow for the formation of soluble flat and curved PAHs containing tetrahydroindeno groups, which could be converted to their fully aromatized analogues with the use of an oxidant.[9]

Scheme 1. New Process To Create Structurally Diverse Tetrahydroindeno-Annulated PAHs



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RESULTS AND DISCUSSION

Our study began with the optimization of the palladium-catalyzed cross-coupling[12] reaction of cyclohexanone with various structurally diverse brominated PAHs **1a–f** (Figure 1).

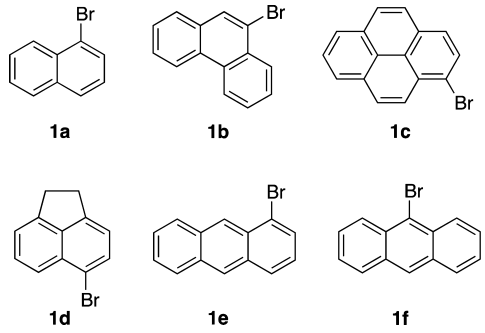
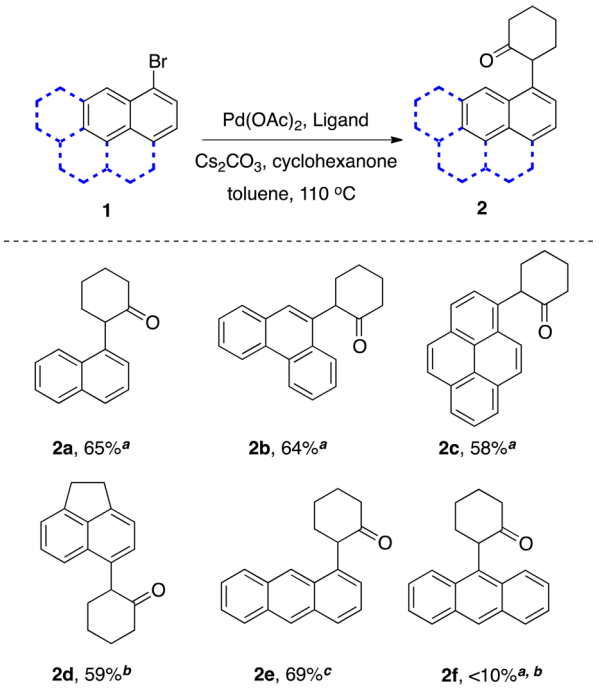


Figure 1. Brominated PAHs investigated in this study.

Reaction conditions that utilized 3–6 mol % of $Pd(OAc)_2$, 7.5–15 mol % of either S-Phos or X-Phos as the ligand, and 1 mol equiv of Cs_2CO_3 as a base in anhydrous toluene at 110–115 °C afforded the best results, providing α-arylated ketones **2a–e**[14] from brominated PAHs **1a–e** in good yields ranging from 54 to 69% (Scheme 2). The cross-coupling of 9-bromoanthracene (**1f**) with cyclohexanone failed to yield α-arylated ketone **2f** in any appreciable amounts under various reaction conditions. We attribute this failure to the sterically hindered environment around the bromine, as 1-bromoanthracene (**1e**) reacts smoothly under the optimized conditions to yield α-arylated ketone **2e** in a 69% isolated yield. Due to the extremely low yield of ketone **2f**, we chose not to continue to examine this substrate in further transformations. Ketones **2a**,**b**,**d** crystallized after purification, allowing for X-ray crystal structures to be determined for these compounds (see the Supporting Information).

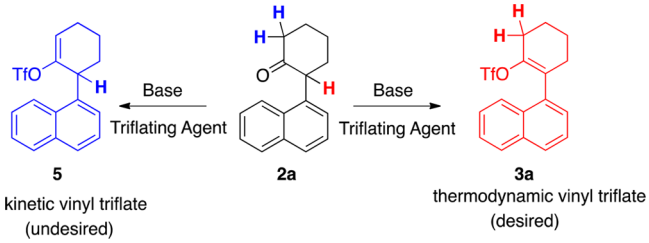
Scheme 2. Substrate Scope of the Palladium-Catalyzed Cross-Coupling of Brominated PAHs with Cyclohexanone To Produce α-Arylated Ketones 2a–f



[a]Conditions: 3 mol % of $Pd(OAc)_2$, 7.5 mol % of S-Phos, 1.5 equiv of cyclohexanone, 1 equiv of Cs_2CO_3, toluene (anhydrous). [b]Conditions: 3 mol % of $Pd(OAc)_2$, 7.5 mol % of X-Phos, 1.5 equiv of cyclohexanone, 1 equiv of Cs_2CO_3, toluene (anhydrous). [c]Conditions: 6 mol % of $Pd(OAc)_2$, 15 mol % of X-Phos, 1.5 equiv of cyclohexanone, 1 equiv of Cs_2CO_3, toluene (anhydrous).

For annulation to be possible, the ketone in compounds **2a–e** must be converted to a functional group that is more amenable for metal-catalyzed cyclization. Our choice was to convert this ketone to a vinyl triflate through the capture of an enolate with a triflating agent.[15] Examining ketone **2a**, it can be observed that there are two possible sites for deprotonation, yielding either the desired thermodynamic vinyl triflate **3a** (highlighted in red) or the undesired kinetic vinyl triflate **5** (highlighted in blue) (Scheme 3).

Scheme 3. Two Possible Vinyl Triflates Produced after Deprotonation of α-Arylated Ketone 2a



Our investigation into conditions that would create the thermodynamic vinyl triflates of ketones **2a–e** was accomplished using α-arylated ketone **2a** as a model system. We began using *N*-phenylbis(trifluoromethanesulfonimide) (triflimide) as the triflating agent and strong bases such as potassium hexamethyldisilazane (KHMDS) and sodium hydride (NaH) in tetrahydrofuran (THF) as the solvent. These reactions produced the undesired kinetic vinyl triflate **5** or no reaction in the case of NaH. Holton and Kraft reported that bromomagnesium diisopropylamide (BMDA)[16] was effective in the production of thermodynamic silyl-enol ethers in substituted cyclohexanones; however, when this method was attempted on our system, it failed to yield the desired isomer **3a**.

Our focus then shifted to weaker alkoxide bases that should be more able to establish an equilibrium, allowing for the selective formation of the desired vinyl triflate **3a**. Sodium ethoxide proved to be sparingly soluble in organic solvents such as dichloromethane (DCM) and tetrahydrofuran (THF) and yielded very little of either regioisomers of the vinyl triflate. We then explored potassium *tert*-butoxide's ability to create **3a**. Attempts to use potassium *tert*-butoxide in anhydrous THF did produce a small amount of the desired **3a** but catalyzed numerous side reactions, producing countless byproducts. We also examined anhydrous DCM as the solvent and found that only the desired thermodynamic vinyl triflate **3a** was produced. Further optimization showed that 3 mol equiv of *tert*-butoxide and 1 mol equiv of triflimide added dropwise produced the best results and gave **3a** in a 77% isolated yield.

Despite the success of these conditions on **2a** to produce **3a**, expansion of this method to ketones **2b–e** proved to be impractical, as the separation of the desired vinyl triflates from the amine byproduct of triflimide was not possible. To rectify

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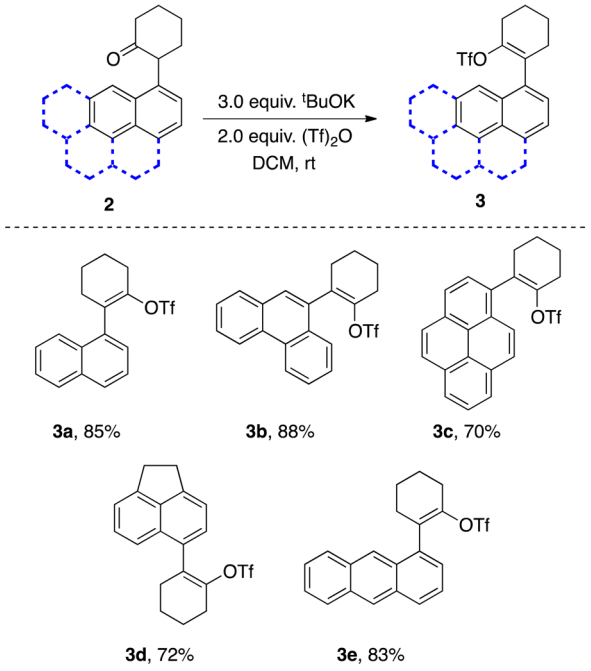
this issue, we changed the triflating agent to triflic anhydride and found that **2a** could be converted to vinyl triflate **3a** in an 85% isolated yield. These conditions were widely applicable and smoothly converted **2b–e** to their corresponding vinyl triflates **3b–e** with 3 equiv of potassium *tert*-butoxide and 2 equiv of triflic anhydride (added dropwise) in anhydrous DCM. The yields of vinyl triflate formation were excellent and ranged from 70 to 88% (Scheme 4). One of the greatest benefits of these

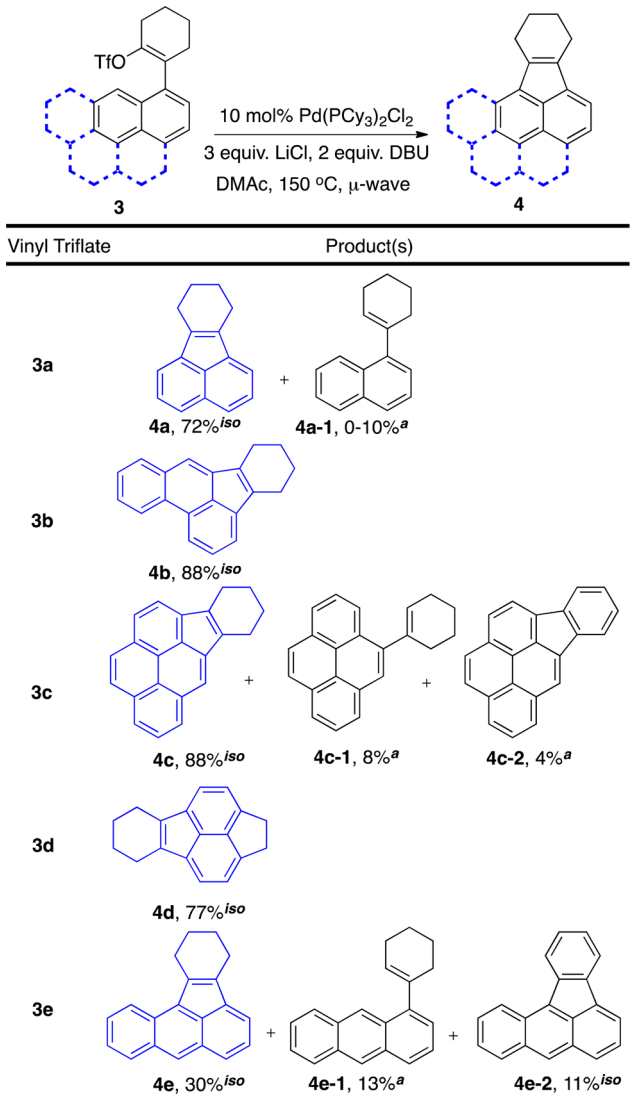
Scheme 4. Substrate Scope for the Conversion of α-Arylated Ketones 2a–e to Vinyl Triflates 3a–e using Optimized Reaction Conditions



reactions is they are self-indicating, as the solution of potassium *tert*-butoxide and **2a–e** undergoes a color change, which is persistent until all of the ketone has been consumed to produce vinyl triflates **3a–e**.

With vinyl triflates in hand, the palladium-catalyzed closure of compounds **3a–e** was investigated under microwave irradiation conditions using a variant[11d,e] of the arene–triflate coupling method developed by Rice and co-workers.[10] Optimization of the arene–vinyl triflate coupling was accomplished by examining the amount of time that was needed for this reaction to go to completion, the temperature, the amount of LiCl that was needed, catalyst loading, and if the reaction could be set up on the benchtop or in an inert-atmosphere glovebag. We chose to use $Pd(PCy_3)_2Cl_2$ as the catalyst for the arene–vinyl triflate coupling because it is an electron-rich catalyst that would allow for facile oxidative addition into the alkene–triflate bond and because it has a proven track record to efficiently catalyze the σ-bond metathesis on numerous strained PAHs.[11d–g] We found that the best results were obtained by the use of 10 mol % of $Pd(PCy_3)_2Cl_2$ and 3 equiv of LiCl, which were added to the microwave vessel in an inert-atmosphere glovebag. Once the solids had been added, the vessel was capped and removed from the glovebag, at which point 2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and anhydrous *N,N*-dimethylacetamide (DMAc) were added and the reaction mixture was heated under microwave irradiation at 150 °C, at 200 W maximum power for 1 h. Vinyl triflates **3a–e** were successfully closed to provide annulated PAHs **4a–e** in yields ranging from 30 to 88%, and the reaction can be run on a larger scale, as demonstrated by the cyclization of **3d** to **4d**, which was run on a near 2.0 mmol scale (Scheme 5).

Scheme 5. Substrate Scope of the Optimized Palladium-Catalyzed Intramolecular Arene–Vinyl Triflate Coupling



[a]Percentages were determined by GC integration. Yields reported for **4a–e** were obtained using the following optimized reaction conditions: 10 mol % of $Pd(PCy_3)_2Cl_2$ and 3 equiv of LiCl, added in an inert-atmosphere glovebag, 2 equiv of DBU, and anhydrous DMAc as the solvent with heating under microwave irradiation at 150 °C, at 200 W maximum power for 1 h.

The arene–vinyl triflate coupling to produce substrates **4a,c,e** occasionally suffered from a minor amount of reductive detriflation (ca. 9–20%) to yield the open products **4a-1**, **4c-1**, and **4e-1**. This reductive detriflation can be attributed to trace amounts of water introduced by the very hygroscopic LiCl. To test this hypothesis, we ran two arene–vinyl triflate coupling reactions on compound **3a**: in one we added 0.50 equiv of water, and in the second we allowed the LiCl to be exposed to air for 5 min. Both produced exclusively the detriflated product

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4a-1.[17] Arene−vinyl triflate couplings to yield compounds **4c,e** also showed aromatization of the saturated ring, producing fully aromatized compounds **4c-2** and **4e-2**, which we believe stems from the presence of oxygen in the reaction.[18] To solve the detriflation and aromatization issues, reactions were set up in a glovebag to eliminate most traces of water and oxygen, which proved fruitful, as this drastically reduced the amount of detriflated and aromatic products. Anthracene vinyl triflate **3e** was our lowest-yielding closure at 30%; while GC/MS analysis of the crude reaction mixture showed only **4e** and **4e-2**, ^{1}H NMR analysis of this arene−vinyl triflate coupling showed a plethora of other side products. We believe that the low yield can be attributed to the same steric issue seen in the failed cross-coupling of 9-bromoanthracene (**1f**). We believe that the closure of **3e** to **4e** is sterically encumbered by the hydrogen in the 8-position of anthracene, which then encourages the formation of side products.

CONCLUSION

In summary, we have developed a new efficient three-step process to annulate polycyclic aromatic hydrocarbons (PAHs) that has been used to create structurally diverse tetrahydroindenoannulated PAHs. Our process utilizes a palladium-catalyzed cross-coupling of brominated aromatic compounds with cyclohexanone to yield α-arylated ketones. These ketones can be regioselectively enolized with potassium *tert*-butoxide and captured by triflic anhydride to give regiospecific vinyl trfilates in good to excellent yields. These vinyl triflates can then undergo an intramolecular palladium-catalyzed arene−vinyl triflate coupling reaction to form tetrahydroindenoannulated PAHs that can be run on a preparative scale. This process provides access to PAHs with saturated rings that under current chemical methods would be difficult to produce in an efficient manner and could be used as an alternate route to various PAHs.

EXPERIMENTAL SECTION

General Experimental Considerations. Anhydrous toluene, dichloromethane, and *N*,*N*-dimethylacetamide were purchased from Acros, and the bottles were equipped with an Acros seal. Cyclohexanone and 1-bromonaphthalene were dried over anhydrous magnesium sulfate at 100 °C for 1 h and then distilled. Cyclohexanone, 1-bromonaphthalene, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were stored over molecular sieves under nitrogen. All solvents, cyclohexanone, and 1-bromonaphthalene were purged with nitrogen before use. Lithium chloride (anhydrous) was stored in a glovebag under nitrogen with desiccant to keep it dry. The palladium-catalyzed annulations were performed in a CEM Discovery Microwave in a sealed vessel with a constant temperature of 150 °C, measured by an external sensor, for 60 min. Proton NMR chemical shifts are reported in ppm downfield from tetramethylsilane with deuterochloroform (δ 7.26 ppm) as the reference standard, unless otherwise specified. Carbon NMR shifts are reported in ppm downfield from tetramethylsilane with deuterochloroform (δ 77.16 ppm) as the reference standard. For column chromatography, silica gel 32−63 μm was used. High-resolution mass spectra (HRMS) were measured using time-of-flight (TOF) mass spectrometry with ionization occurring either with electron impact (EI) or liquid introduction field desorption ionization (LIFDI).

General Procedure for the Synthesis of Compounds 2a−d. An oven-dried 10 mL pressure vessel containing a Teflon-coated stir bar was charged with 2.0 mmol of a brominated polycyclic aromatic hydrocarbon (PAH), $Pd(OAc)_2$ (13 mg, 0.06 mmol), S-Phos (62 mg, 0.15 mmol) or X-Phos (72 mg, 0.15 mmol), and anhydrous Cs_2CO_3 (660 mg, 2.0 mmol). The tube was capped with a rubber septum equipped with a vent needle, and it was flushed with nitrogen for 15 min. Cyclohexanone (290 mg, 3.0 mmol) and 2.0 mL of toluene (anhydrous) were added via a syringe through the septum. The septum was removed under a constant nitrogen flow and capped with a Teflon screw cap. The reaction was stirred at room temperature for 10 min. After 10 min the pressure vessel was heated with stirring in an oil bath at 110 °C for 20−26 h. Upon completion, the reaction mixture was cooled to room temperature, diluted with dichloromethane, and poured into a separatory funnel, where the organic layer was washed three times with 1 M HCl. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Purification of the residue was accomplished by column chromatography using silica gel with hexanes and ethyl acetate as the eluent.

*2-(Naphthalen-1-yl)cyclohexanone (**2a**).* The reaction was run with S-Phos as the ligand. Purification was accomplished with a 10/1 hexanes/ethyl acetate solvent mixture, which yielded 292 mg (65%) of a white solid: mp 71−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.86 (m, 1H), 7.80 (d, J = 8.3, 1H), 7.76−7.72 (m, 1H), 7.51−7.45 (m, 3H), 7.38 (d, J = 7.2, 1H), 4.38 (dd, J = 12.5, 5.3 Hz, 1H), 2.73−2.62 (m, 2H), 2.48−2.40 (m, 1H), 2.36−2.24 (m, 2H), 2.19−2.12 (m, 1H), 2.04−1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 135.2, 133.8, 131.8, 129.0, 127.6, 125.9, 125.4, 125.37, 125.34, 123.30, 53.4, 42.7, 34.3, 27.9, 26.0; IR (KBr) 1708 cm^{-1} (C═O); HRMS (EI, m/z) calcd for $C_{16}H_{16}O$ (M^+) 224.1201, found 224.1202.

*2-(Phenanthren-9-yl)cyclohexanone (**2b**).* The reaction was run with S-Phos as the ligand. Purification was accomplished with a 10/1 hexanes/ethyl acetate solvent mixture, which yielded 351 mg (64%) of a white solid: mp 145−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.0, 1H), 8.68 (d, J = 8.1 Hz, 1H), 7.86 (dd, J = 7.8, 1.6 Hz, 1H), 7.75 (dd, J = 8.2, 1.4 Hz, 1H), 7.70−7.54 (m, 5H), 4.41 (dd, J = 12.5, 5.1 Hz, 1H), 2.78−2.63 (m, 2H), 2.59−2.49 (m, 1H), 2.48−2.35 (m, 1H), 2.35−2.27 (m, 1H), 2.25−2.16 (m, 1H), 2.08−1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 133.6, 131.5, 130.9, 130.7, 130.0, 128.5, 126.6, 126.5, 126.4, 126.10, 126.08, 124.0, 123.4, 122.4, 53.6, 42.8, 33.9, 28.1, 26.0; IR (KBr) 1704 cm^{-1} (C═O); HRMS (EI, m/z) calcd for $C_{20}H_{18}O$ (M^+) 274.1358, found 274.1371.

*2-(Pyren-1-yl)cyclohexanone (**2c**).* The reaction was run with S-Phos as the ligand. Purification was accomplished with a 10/1 hexanes/ethyl acetate solvent mixture, which yielded 346 mg (58%) of a white solid: mp 123−125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 2H), 8.19−8.16 (m, 1H), 8.14−8.05 (m, 3H), 8.05−7.98 (m, 2H), 7.91 (d, J = 8.0 Hz, 1H), 4.68 (dd, J = 12.6, 5.5 Hz, 1H), 2.81−2.68 (m, 2H), 2.60−2.50 (m, 1H), 2.50−2.40 (m, 1H), 2.40−2.29 (m, 1H), 2.27−2.14 (m, 1H), 2.14−1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 133.6, 131.5, 130.9, 130.7, 130.0, 128.5, 126.6, 126.47, 126.46, 126.10, 126.08, 126.07, 124.0, 123.4, 122.4, 53.6, 42.8, 33.9, 28.1, 26.0; IR (KBr) 1704 cm^{-1} (C═O); HRMS (EI, m/z) calcd for $C_{22}H_{18}O$ (M^+) 298.1358, found 298.1368.

*2-(Acenaphthen-5-yl)cyclohexanone (**2d**).* The reaction was run with X-Phos as the ligand. Purification of the residue was accomplished by column chromatography using silica gel with hexanes and ethyl acetate (11/1) as the eluent; yielding 297 mg (59%) of a white solid: mp 99−102 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.50−7.43 (m, 2H), 7.36−7.29 (m, 3H), 4.27 (dd, J = 12.7, 5.5 Hz, 1H), 3.50−3.38 (m, 4H), 2.74−2.55 (m, 2H), 2.46−2.37 (m, 1H), 2.37−2.25 (m, 2H), 2.20−2.10 (m, 1H), 2.06−1.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 146.7, 145.2, 139.5, 131.0, 130.3, 127.6, 126.9, 119.0, 53.14, 42.5, 34.4, 30.5, 29.9, 27.8, 25.9; IR (KBr) 1708 cm^{-1} (C═O); HRMS (EI, m/z) calcd for $C_{18}H_{18}O$ (M^+) 250.1358, found 250.1363.

2-(Anthracen-1-yl)cyclohexanone (2e). An oven-dried 10 mL pressure vessel containing a Teflon-coated stir bar was charged with 2.0 mmol of 1-bromoanthracene (**1e**), $Pd(OAc)_2$ (24 mg, 0.12 mmol), X-Phos (140 mg, 0.30 mmol), and anhydrous Cs_2CO_3 (660 mg, 2.0 mmol). The tube was capped with a rubber septum equipped with a vent needle, and it was flushed with nitrogen for 15 min. Cyclohexanone (290 mg, 3.0 mmol) and 2.0 mL of toluene (anhydrous) were added via a syringe through the septum. The septum was removed under a constant nitrogen flow and capped with a Teflon screw cap. The reaction mixture was stirred at room

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temperature for 10 min. After 10 min, the pressure vessel was heated with stirring in an oil bath at 110 °C for 72 h. Upon completion, the reaction mixture was cooled to room temperature, diluted with dichloromethane, and poured into a separatory funnel, where the organic layer was washed three times with 1 M HCl. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Purification of the residue was accomplished by column chromatography using silica gel with hexanes and ethyl acetate (10/1) as the eluent, yielding 379 mg (69%) of a white solid: mp 136−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.27 (s, 1H), 8.09−7.93 (m, 3H), 7.52−7.41 (m, 3H), 7.37 (d, J = 6.9 Hz, 1H), 4.56 (dd, J = 12.4, 5.2 Hz, 1H), 2.84−2.65 (m, 2H), 2.56−2.45 (m, 1H), 2.44−2.28 (m, 2H), 2.25−2.14 (m, 1H), 2.12−1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 135.2, 132.1, 131.5, 131.2, 130.4, 128.5, 128.0, 127.8, 127.3, 125.39, 125.38, 124.8, 124.7, 121.8, 53.4, 42.8, 34.3, 28.1, 26.0; IR (KBr) 1699 cm^{-1} (C═O); HRMS (EI, m/z) calcd for $C_{20}H_{18}O$ (M^+) 274.1358, found 274.1357.

General Procedure for the Synthesis of Compounds 3a−e. An oven-dried 20 mL scintillation vial containing a Teflon-coated stir bar was charged with 0.5 mmol of one of the arylated ketones **2a−e** and 168 mg (1.5 mmol) of potassium *tert*-butoxide and then capped with a septum. The vial was flushed with N_2 for 5 min. To this mixture of solids was added 8.0 mL of anhydrous dichloromethane (DCM) via a syringe, which caused an immediate color change. The reaction mixture was stirred at room temperature for 10 min. After 10 min of stirring, triflic anhydride was added dropwise (via a syringe) until the color disappeared (ca. 0.17 mL, 1.0 mmol). After the last drop of triflic anhydride was added, the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was poured into a separatory funnel, diluted with dichloromethane, washed with 1 M HCl (three times), and separated. The organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Purification was accomplished by silica gel chromatography with hexanes and ethyl acetate or DCM as the eluent.

*2-(Naphthalen-1-yl)cyclohex-1-en-1-yl Trifluoromethanesulfonate (**3a**).* Purification was accomplished with a 9/1 hexanes/ethyl acetate solvent mixture, which yielded 280 mg (85%) of a white solid: mp 59−61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.89 (m, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.85−7.79 (m, 1H), 7.60−7.50 (m, 3H), 7.38 (dd, J = 7.0, 1.2 Hz, 1H), 2.73−2.58 (m, 3H), 2.57−2.46 (m, 1H), 2.10−2.00 (m, 2H), 1.97−1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 134.7, 133.7, 130.5, 128.5, 128.3, 126.2, 125.9, 125.3, 124.8, (CF_3, 122.8, 119.6, 116.4, 113.2), 32.0, 27.9, 23.2, 22.1; HRMS (EI, m/z) calcd for $C_{17}H_{15}F_3O_3S$ (M^+) 356.0694, found 356.0703.

*2-(Phenanthren-9-yl)cyclohex-1-en-1-yl Trifluoromethanesulfonate (**3b**).* Purification was accomplished with a 10/1 hexanes/ethyl acetate solvent mixture, which yielded 166 mg (88%) of a white solid: mp 110−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 8.1 Hz, 1H), 8.73 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.75−7.61 (m, 5H), 2.78−2.59 (m, 4H), 2.59−2.44 (m, 1H), 2.16−1.97 (m, 2H), 1.98−1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 133.3, 131.3, 130.6, 130.5, 130.1, 129.4, 128.7, 126.9, 126.80, 126.78, 126.70, 126.66, 125.5, 123.1, 122.6, (CF_3, 122.7, 119.6, 116.4, 113.2), 31.9, 27.9, 23.3, 22.1; HRMS (EI, m/z) calcd for $C_{21}H_{17}F_3O_3S$ (M^+) 406.0851, found 406.0866.

*2-(Pyren-1-yl)cyclohex-1-en-1-yl Trifluoromethanesulfonate (**3c**).* Purification was accomplished with a 1/1 hexanes/DCM solvent mixture, which yielded 150 mg (70%) of a white solid: mp 123−125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28−8.18 (m, 3H), 8.17−8.08 (m, 3H), 8.07−7.99 (m, 2H), 7.84 (d, J = 7.9 Hz, 1H), 2.76−2.62 (m, 4H), 2.16−2.06 (m, 2H), 2.04−1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 132.1, 131.3, 131.0, 130.9, 128.0, 127.8, 127.6, 127.4, 126.1, 126.0, 125.4, 125.2, 124.9, 124.81, 124.76, 124.3, (CF_3, 122.7, 119.5, 116.4, 113.2), 32.6, 28.1, 23.3, 22.2; HRMS (LIFDI, m/z) calcd for $C_{23}H_{17}F_3O_3S$ (M^+) 430.0851, found 430.0861.

*2-(1,2-Dihydroacenaphthylen-5-yl)cyclohex-1-en-1-yl Trifluoromethanesulfonate (**3d**).* An oven-dried 50 mL round-bottom flask containing a Teflon-coated stir bar was charged with 0.68 g (2.7 mmol) of ketone **2d** and 0.91 g (8.1 mmol) of potassium *tert*-butoxide and then capped with a septum. The round-bottom flask was flushed with N_2 for 5 min. To this mixture of solids was added 20 mL of anhydrous dichloromethane via a syringe, which caused an immediate color change. The reaction mixture was stirred at room temperature for 10 min. An oven-dried pear-shaped flask, fitted with a septum, was charged with 1.5 g (5.4 mmol, 0.91 mL) of triflic anhydride and 5.0 mL of anhydrous dichloromethane. After 10 min of stirring, triflic anhydride/DCM solution was added dropwise to the reaction (via a syringe) until the color disappeared. After the last drop of triflic anhydride was added, the reaction mixture was stirred at room temperature for 1 h. The reaction was poured into a separatory funnel, diluted with dichloromethane, washed with 1 M HCl (three times), and separated. The organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure.

Purification was accomplished by column chromatography using silica gel with a 9/1 hexanes/ethyl acetate solvent mixture, which yielded 756 mg (72%) of a colorless tacky solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.54−7.47 (m, 2H), 7.39−7.28 (m, 3H), 3.50−3.40 (m, 4H), 2.66−2.45 (m, 4H), 2.02 (p, J = 6.0 Hz, 2H), 1.88 (p, J = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 146.3, 144.6, 139.4, 130.1, 130.0, 128.9, 128.0, 127.7, 120.0, 119.4, 118.8, (CF_3, 122.8, 119.6, 116.4, 113.4), 31.9, 30.5, 30.1, 27.9, 23.3, 22.2; HRMS (EI, m/z) calcd for $C_{19}H_{17}F_3O_3S$ (M^+) 382.0851, found 382.0841.

*2-(Anthracen-1-yl)cyclohex-1-en-1-yl Trifluoromethanesulfonate (**3e**).* Purification was accomplished with a 1/1 hexanes/DCM solvent mixture, which yielded 169 mg (83%) of a pale yellow tacky solid: ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.49 (s, 1H), 8.35 (s, 1H), 8.12−8.00 (m, 3H), 7.58−7.47 (m, 3H), 7.37 (d, J = 6.7 Hz, 1H), 2.81−2.61 (m, 3H), 2.61−2.49 (m, 1H), 2.20−2.04 (m, 2H), 2.03−1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 134.8, 131.8, 131.7, 131.6, 130.6, 128.8, 128.6, 128.4, 128.0, 127.0, 125.6, 125.5, 125.4, 124.6, 123.4, (CF_3, 119.5, 116.3), 31.9, 27.9, 23.3, 22.2; HRMS (EI, m/z) calcd for $C_{21}H_{17}F_3O_3S$ (M^+) 406.0851, found 406.0872.

General Procedure for the Synthesis of Compounds 4a−e. Vinyl triflates **3a−e** were transferred to an oven-dried 15 mL pear-shaped flask with anhydrous dichloromethane. The solvent was removed under reduced pressure, and the flask was kept under vacuum for at least 5 h. After 5 h the flask was fitted with a septum and flushed with nitrogen for 10 min. In a glovebag (that had been evacuated and filled with dry high-purity nitrogen three times) a 10 mL oven-dried CEM Corporation microwave vessel was charged with 10 mol % of $Pd(PCy_3)_2Cl_2$ and 3.0 mol equiv of LiCl (anhydrous) and the vessel was capped with a CEM septum pressure cap, removed from the glovebag, and kept under nitrogen. The pear-shaped flask containing the vinyl triflate was charged with 2.0 mL of anhydrous *N*,*N*-dimethylacetamide (DMAc) (that had been purged with dry nitrogen for 20 min) under nitrogen via a syringe. When all of the vinyl triflate was dissolved, this mixture was transferred to the microwave vessel along with 2.0 mol equiv of anhydrous 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) via a syringe and the reaction mixture was stirred at room temperature for 10 min. After 10 min, the reaction mixture was subjected to microwave irradiation in a CEM Discoverer Microwave Unit at a temperature of 150 °C with a maximum power of 200 W for 1 h. Upon completion, the vessel was removed from the microwave and the reaction mixture was diluted with dichloromethane and poured into a separatory funnel, where it was rinsed (three times) with 1 M HCl. The organic layer was separated, dried with anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified either with flash column chromatography or preparative TLC with hexanes and ethyl acetate or DCM as the eluent.

*7,8,9,10-Tetrahydrofluoranthene (**4a**).* Arene−vinyl triflate coupling was run with 150 mg (0.42 mmol) of vinyl triflate **3a**, 31 mg (0.042 mmol, 10 mol %) of $Pd(PCy_3)_2Cl_2$, 54 mg (1.3 mmol, 3.0 equiv) of LiCl, and 130 mg (0.84 mmol, 2.0 equiv) of DBU. Purification on flash column chromatography was accomplished with 19/1 hexanes/ethyl acetate to produce 60 mg of a yellow solid in 72% yield: mp 73−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.67 (m, 2H), 7.52−7.47 (m, 4H), 2.80−2.75 (m, 4H), 1.98−1.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 136.9, 128.8, 127.7, 127.4, 126.1,

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120.1, 22.9, 22.8; HRMS (EI, m/z) calcd for $C_{16}H_{14}$ (M^+) 206.1096, found 206.1093.

*9,10,11,12-Tetrahydrobenzo[e]acephenanthrylene (**4b**).* Arene−vinyl triflate coupling was run with 79 mg (0.19 mmol) of vinyl triflate **3b**, 14 mg (0.019 mmol, 10 mol %) of $Pd(PCy_3)_2Cl_2$, 25 mg (0.58 mmol, 3.0 equiv) of LiCl, and 59 mg (0.39 mmol, 2.0 equiv) of DBU. Purification on flash column chromatography was accomplished with 19/1 hexanes/ethyl acetate to produce 44 mg of a yellow solid in 88% yield: decomposition began at 56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.75 (s, 1H), 7.68−7.55 (m, 3H), 7.48 (d, J = 6.9 Hz, 1H), 2.81−2.76 (m, 4H), 2.00−1.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 140.0, 138.9, 135.8, 134.3, 130.9, 130.1, 129.4, 127.6, 126.7, 126.3, 125.3, 123.1, 121.5, 120.4, 118.7, 23.0, 22.9, 22.8, 22.7; HRMS (EI, m/z) calcd for $C_{20}H_{16}$ (M^+) 256.1252, found 256.1251.

*7,8,9,10-Tetrahydroindeno[1,2,3-cd]pyrene (**4c**).* Arene−vinyl triflate coupling was run with 75 mg (0.17 mmol) of vinyl triflate **3c**, 13 mg (0.017 mmol, 10 mol %) of $Pd(PCy_3)_2Cl_2$, 22 mg (0.51 mmol, 3.0 equiv) of LiCl, and 52 mg (0.34 mmol, 2.0 equiv) of DBU. Purification on preparative TLC was accomplished with 9/1 hexanes/DCM to produce 42 mg of a red solid in 88% yield: decomposition began at 79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.7 Hz, 1H), 8.22 (d, J = 7.7 Hz, 1H), 8.13 (s, 1H), 8.08−8.04 (m, 2H), 8.02−7.96 (m, 2H), 7.93 (d, J = 8.3 Hz, 2H), 2.95−2.93 (m, 4H), 2.04−2.01 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 139.6, 136.3, 135.4, 132.0, 130.01, 129.97, 129.4, 127.45, 127.39, 126.7, 126.17, 126.14, 123.8, 122.2, 121.6, 120.1, 119.2, 23.6, 23.0, 23.00, 22.97. HRMS (EI, m/z) calcd for $C_{22}H_{16}$ (M^+) 280.1252, found 280.1259.

*1,2,5,6,7,8-Hexahydrocyclopenta[cd]fluoranthene (**4d**).* Arene−vinyl triflate coupling was run with 756 mg (1.98 mmol) of vinyl triflate **3d**, 223 mg (0.198 mmol, 10 mol %) of $Pd(PCy_3)_2Cl_2$, 384 mg (5.94 mmol, 3.0 equiv) of LiCl, 919 mg (6.04 mmol, 2.0 equiv) of DBU, and 5.0 mL of anhydrous DMAc. Purification on flash column chromatography was accomplished with 19/1 hexanes/ethyl acetate to produce 355 mg of a yellow solid in 77% yield: decomposition began at 100 °C; ^{1}H NMR (400 MHz, chloroform-d) δ 7.53 (d, J = 6.8 Hz, 2H), 7.32 (d, J = 6.7 Hz, 2H), 3.47 (s, 4H), 2.86−2.80 (m, 4H), 1.95−1.90 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 136.5, 136.2, 134.6, 127.2, 122.1, 120.1, 32.3, 23.7, 23.1; HRMS (EI, m/z) calcd for $C_{18}H_{16}$ (M^+) 232.1252, found 232.1244.

*1,2,3,4-Tetrahydrobenzo[a]aceanthrylene (**4e**).* Arene−vinyl triflate coupling was run with 75 mg (0.18 mmol) of vinyl triflate **3e**, 13 mg (0.018 mmol, 10 mol %) of $Pd(PCy_3)_2Cl_2$, 23 mg (0.54 mmol, 3.0 equiv) of LiCl, and 55 mg (0.36 mmol, 2.0 equiv) of DBU. Purification on preparative TLC was accomplished with 9/1 hexanes/DCM to produce 14 mg of a red solid in 30% yield: decomposition began at 66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.7 Hz, 1H), 8.32 (s, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.59 (d, J = 6.5 Hz, 1H), 7.55−7.47 (m, 2H), 7.43−7.36 (m, 1H), 3.25 (tt, J = 6.0, 2.8 Hz, 2H), 2.85 (tt, J = 5.8, 2.7 Hz, 2H), 2.09−2.00 (m, 2H), 2.00−1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 138.4, 135.2, 135.0, 134.6, 130.6, 129.1, 127.0, 126.9, 126.9, 126.8, 126.1, 126.0, 124.3, 124.1, 121.3, 26.5, 23.6, 22.9, 22.5; HRMS (EI, m/z) calcd for $C_{20}H_{16}$ (M^+) 256.1252, found 256.1246.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving ^{1}H and ^{13}C NMR spectra for all compounds and crystal structure data for compounds **2a,b,d**. 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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