JOC The Journal of Organic Chemistry

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Synthesis of Functionalized Phenanthrenes via Regioselective Oxidative Radical Cyclization

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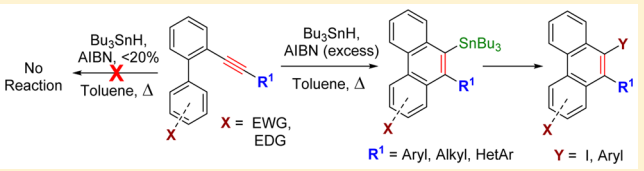
Supporting Information

ABSTRACT: The majority of Sn-mediated cyclizations are reductive and, thus, cannot give a fully conjugated product. This is a limitation in the application of Sn-mediated radical cascades for the preparation of fully conjugated molecules. In this work, we report an oxidatively terminated Bu_3Sn-mediated cyclization of an alkyne where AIBN, the commonly used initiator, takes on a new function as an oxidative agent. Sn-mediated radical transformation of biphenyl aryl acetylenes into functionalized phenanthrenyl stannanes can be initiated via two potentially equilibrating vinyl radicals, one of which can be trapped by the fast 6-endoclosure at the biphenyl moiety in good to excellent yields. The efficient preparation of Sn-substituted phenanthrenes opens access to convenient building blocks for the construction of larger polyaromatics.



INTRODUCTION

In our continuing efforts to expand the synthetic utility of radical cyclizations[1,2] toward the preparation of precisely functionalized and shaped polyaromatic building blocks, we developed multiple ways for taking advantage of carbon-rich character of the alkyne functionality for the preparation of cyclic conjugated molecules.[3] This work addressed the questions of regio- and chemoselectivity of activation and exo/endoselectivity for the ring forming steps. In this work, we address manipulation of the oxidation state of the final products.

In our earlier work, we found that cyclizations of fully conjugated oligoalkynes lead to reduction of two alkyne carbons: the place of initial Sn-attack and the place of final ring closure (Scheme 1). As a result, these sequences form a polycylic system with two partially reduced five-membered rings. In a more recent work, we avoided both the formation of one of the five-membered rings and the partial reduction at the cascade initiation point by utilizing "skipped" oligoalkynes equipped with a traceless directing group.[4] Loss of the directing group proceeds via C−O bond fragmentation driven by aromatization of the top ring in the ribbon (Scheme 1), the process that adjusts the oxidation state and assists in avoiding the reduced product formation. However, the termination point of the cascade still includes a partially reduced five-membered cycle.

Guided by the hypothesis that such reduction can be avoided by terminating the cascade by an oxidizing step, we designed the new radical cascade reported in this work. This cascade features an intermolecular attack at the alkyne that, albeit not necessarily selective itself, can still lead to selective 6-*endo* cyclization followed by an oxidative termination step that uses AIBN, a commonly used radical initiator as an oxidant. This reaction provides a simple and efficient strategy for the synthesis of substituted phenanthrenyl stannanes from 2-(1-alkynyl)-biphenyls via Bu_3SnH/AIBN-mediated radical cyclization. The products are conveniently functionalized for further transformations.

RESULTS AND DISCUSSION

The required starting materials **1a**−**l** are readily prepared from the respective 2-bromobiphenyls via the Sonogashira cross-coupling (Scheme 2). The cross-coupling proceeded in good yields to produce the library of 2-(arylethynyl)biphenyls (**1a**−**l**) in 70−84% yields.

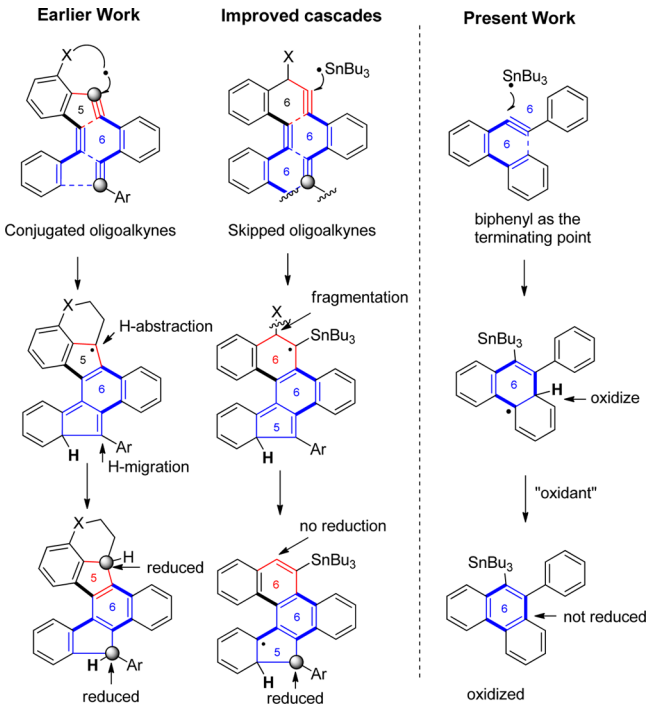
As shown in Table 1, when we tried with 20 mol % of AIBN we did not observe any transformation of **1a** to **2a** (entries 1), we recovered only starting material. Tin-containing reagents (Bu_3SnH/AIBN and Ph_3SnH/AIBN) promote the radical cyclization of substrate **1a** to phenanthrene **2a** in refluxing toluene in good yields (entries 2 and 3). On the contrary, Et_3SiH and $(Me_3Si)_3SiH$ do not transform **1a** into **2a** (entries 5 and 6). We also examined the effect of solvents. Reaction proceeded more efficiently in toluene than in other solvents, such as benzene and THF (65% and 70%, respectively, entries 9 and 10). Once suitable conditions for this transformation were determined, we concentrated our efforts on optimizing the amounts of reagent and initiator. The yields were lower when the amount of Bu_3SnH reagent was reduced to <1.2 mol equiv (entries 14 and 15) or when the amount of initiator was

Special Issue: 50 Years and Counting: The Woodward-Hoffmann Rules in the 21st Century

Received: May 7, 2015

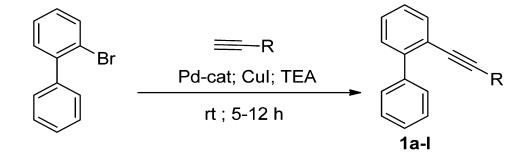
DOI: 10.1021/acs.joc.5b01014
J. Org. Chem. XXXX, XXX, XXX−XXX

Scheme 1. Reductive and Oxidative Sn-Mediated Radical Cascades[a]



[a]Alkyne carbons that will be reduced in the product are indicated with gray circles.

Scheme 2. Synthesis of Requisite 2-(Arylethynyl)biphenyls

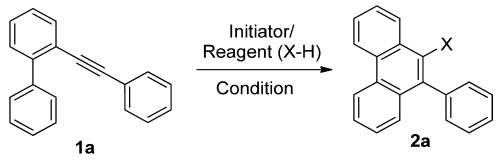


R = Ph, 4-Me-C_6H_5, 4-F-C_6H_5, 4-CN-C_6H_5, 4-CF_3-C_6H_5, naphthyl, n-Bu, 4-OMe-C_6H_5, 4,5-O-CH_2-O-C_6H_4, thiophene, pyridinyl

reduced to <1.0 equiv (entry 16). The relatively high amount of initiator is particularly noteworthy. More than 90% of starting material was recovered when <0.2 equiv of AIBN was used. On the other hand, reaction proceeded to the full conversion with 1.0 equiv of AIBN, providing up to 90% of the phenanthrene product.

With the optimal reaction conditions in hand, we explored the substrate scope of this transformation. We tested the reactions of additional 2-(arylethynyl) biphenyls **1b**–**1i** under the optimized conditions (Table 2). The radical cyclization is fully compatible with acceptor (**1c**–**e** and **1p**) and donor (**1b**, **1h**) substituents at the alkyne termini. The process also tolerates heteroaromatics and alkyl substitution. The corresponding products **2i**–**2m** that incorporate pyridine, thiophene, benzothiophene, and *n*-butyl groups were obtained in high yields (70–81%). Furthermore, alterations at the biphenyl part of the substrate are also possible, i.e., the reaction of benzofuran **1j** gave 70% of 6-(4-methoxyphenyl)-3-methylnaphtho[1,2-*b*]benzofuran **2j**. In a similar manner, reactions of alkynes **1n** and **1o** with additional substitution in the biphenyl moiety provided the respective products **2n** and **2o** in high yields (76% and 82%). These results highlight the broad scope and selectivity of this method.

Table 1. Screening of Reaction Conditions[a]



entry	reagent (equiv)/initiator (equiv)	condition	conversion (%)[b]	yield (%)[c]
1	Bu_3SnH(1.0)/ AIBN(0.2)	toluene, 14 h, 110 °C	–	SM
2	Bu_3SnH(1.5)/ AIBN(1.0)	toluene, 14 h, 110 °C	100	90
3	Ph_3SnH(1.5)/ AIBN(1.0)	toluene, 14 h, 110 °C	100	80
4	no reagent/initiator	toluene, 14 h, 110 °C	0	SM
5	Et_3SiH (1.5)/ AIBN(1.0)	toluene, 14 h, 110 °C	30	–[d]
6	$(Me_3Si)_3SiH$ (1.5)/ AIBN(1.0)	toluene, 14 h, 110 °C	20	–[d]
7	Bu_3SnH (1.5)/ ABCN(1.0)	toluene, 14 h, 110 °C	100	70
8	Bu_3SnH (1.5)/ DTBPB(1.0)	toluene, 14 h, 110 °C	40	60
9	Bu_3SnH(1.5)/ AIBN(1.0)	benzene, 14 h, 80 °C	80	65
10	Bu_3SnH(1.5)/ AIBN(1.0)	THF, 14 h, 66 °C	100	70
11	Bu_3SnH(2.0)/ AIBN(1.0)	Toluene, 14 h, 110 °C	100	90
12	Bu_3SnH(1.8)/ AIBN(1.0)	toluene, 14 h, 110 °C	100	90
13	Bu_3SnH(1.2)/ AIBN(1.0)	toluene, 14 h, 110 °C	100	90
14	Bu_3SnH(1.0)/ AIBN(1.5)	toluene, 14 h, 110 °C	100	70
15	Bu_3SnH(1.0)/ AIBN(1.0)	toluene, 14 h, 110 °C	70	60
16	Bu_3SnH(1.0)/ AIBN(0.5)	toluene, 14 h, 110 °C	40	30
17	Bu_3SnH(0.6)/ AIBN(1.0)	toluene, 14 h, 110 °C	60	40
18	Bu_3SnH(1.5)/Et_3B(1.0)	toluene, 16 h, rt	–	SM

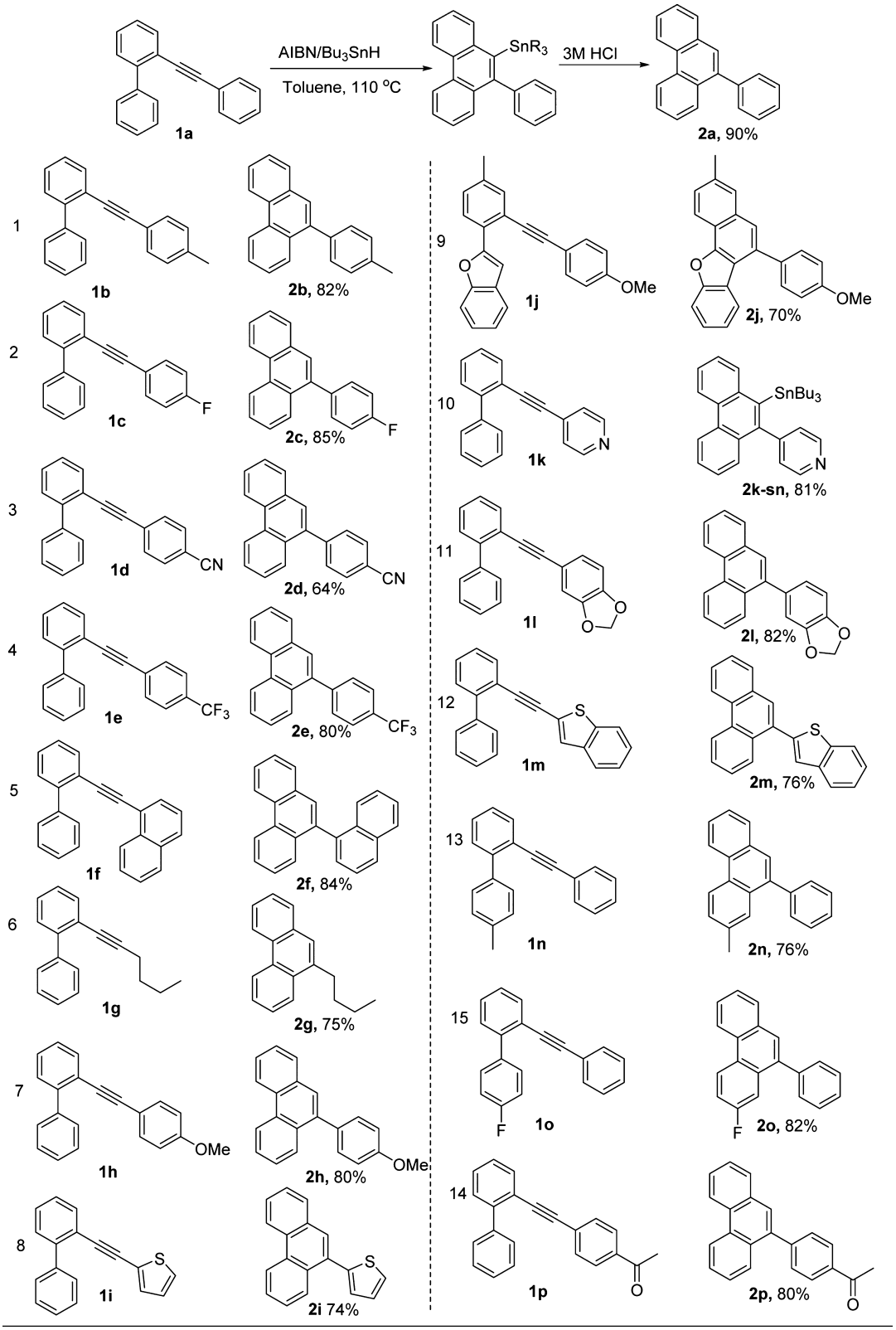
[a]0.04 M concentration of [**1a**] was used unless stated otherwise. SM = starting material. [b]Conversion rate reported based on H NMR. [c]Yields are based on H NMR (see Experimental Section for the details). The product yields are lower than conversion of the starting material due to the formation of small amounts of unidentified side products. [d]Substrate **1a** remained unreacted.

The structure of the products was confirmed with a combination of NMR techniques and in the case of iodinated compound **3a** with X-ray crystallography[5] (Figure 1). The position of iodo-substituent unambiguously confirms the presence and the position of the Sn-moiety.

Computational Details. Potential energy profiles for this cascade transformation were evaluated with Gaussian 09[6] using the UM06-2X functional,[7] capable of relatively accurate description of reaction and activation energies for a variety of chemical processes including radical reactions.[8] The LanL2DZ basis set was used due to the need to study Sn-substituted molecules. Chemcraft 1.7[9] and CYLView[10] were used to render the molecules and orbitals. Frequency calculations were performed to confirm each stationary point as either a minimum or a first-order saddle point. NBO 3.0 program was used to analyze electronic properties of reactive intermediates.[11] The ΔG values for all reactions were calculated at 110

DOI: 10.1021/acs.joc.5b01014
J. Org. Chem. XXXX, XXX, XXX–XXX

Table 2. Radical Cyclization of 2-(1-Arylethynyl)biphenyls[a]



[a]Isolated yields after acid hydrolysis and silica column chromatography. Concentration of ethynyl biphenyls reactants was 0.04M.

°C, the experimental temperature. A truncated version of the attacking radical ($SnMe_3$) was used instead of $SnBu_3$.

Two Sources of Selectivity. The selectivity of the new transformation depends on the two following factors: (a) the selectivity of initial radical attack and (b) the selectivity of the subsequent cyclizations. In order to understand the origin for the exclusive attack at the carbon adjacent to the biphenyl moiety, we evaluated the activation barriers for the two

DOI: 10.1021/acs.joc.5b01014
J. Org. Chem. XXXX, XXX, XXX−XXX

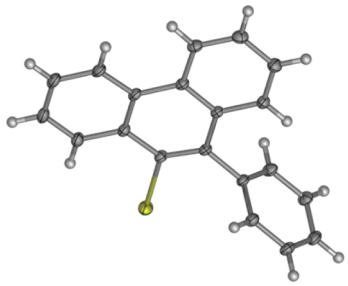
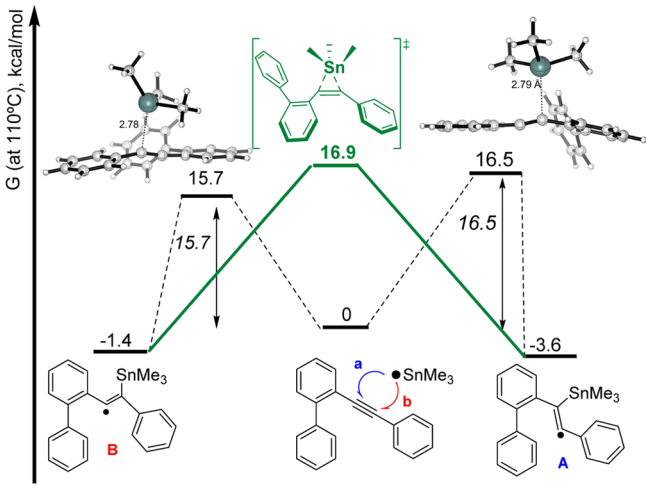


Figure 1. ORTEP for **3a** (50%).

alternative intermolecular attack directions (Scheme 3). Interestingly, at the present level of theory, the formation of

Scheme 3. Potential Energy Diagram for the Formation of Radicals A and B from the Biphenyl Phenyl Alkyne



"unproductive" radical **B** is predicted to be marginally faster ($\Delta\Delta G^{\ddagger}$ 0.8 kcal/mol). However, the "productive" radical **A** is also predicted to be 2.2 kcal/mol more stable than radical **B**. Formation of both radicals is only weakly exergonic and can be considered reversible under the reaction conditions.

Because the transformation of unproductive radical **B** to the productive radical **A** is exergonic, we have also explored the additional ways that can take advantage of the well-known weakness of C−Sn bonds for interconverting the two radicals. The additional analysis identified a radical 1,2-Sn-shift as a feasible direct route for formation of the productive radical **A** directly from the unproductive radical **B**. Figure 2 illustrates geometry for the 1,2-shift transition state (TS). Due to the

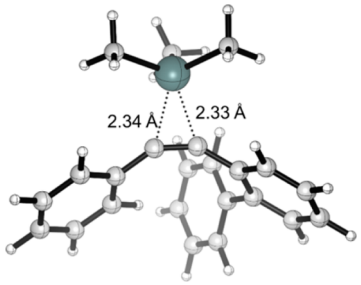


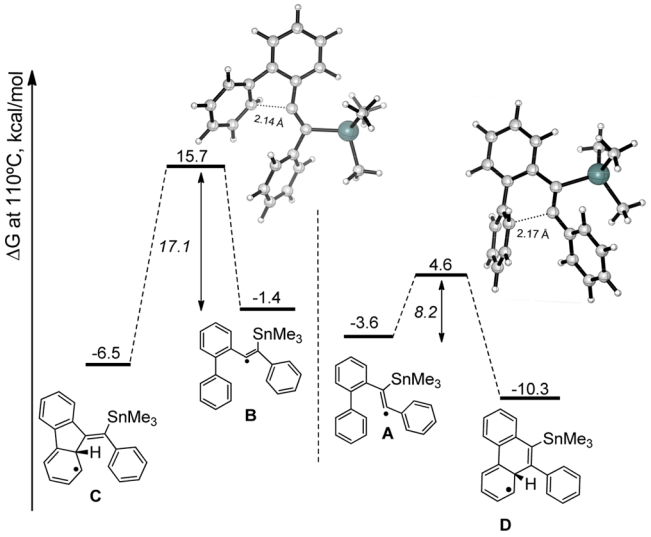
Figure 2. TS geometry for 1,2-Sn shift that interconverts the two vinyl radicals.

relatively low accuracy of the presently available computational methods, the absolute energy for the 1,2-shift TS (16.9 kcal/mol) and the TS leading to the direct formation of radical **A** from the alkyne reactant (16.5 kcal/mol) should be considered, within the computational margin of error, as identical. For comparison, we had also calculated activation energy for the analogous shift of the $SiMe_3$ (TMS) group and found that the respective 1,2-shift TS lies much higher (27.0 kcal/mol higher than the alkyne and TMS radical and 41.5 kcal/mol higher than the Si-analogue of radical **B**, see the Supporting Information).

The situation where radicals are dynamically interconverted via relatively fast reactions can be referred to as "a pool of radicals".[12] When coupled with kinetic self-sorting via a low barrier irreversible reaction, this kinetic scenario provides an unorthodox approach to the control of radical processes that provides a convenient alternative to the use of electronic effects[13] and traceless directing groups.[4]

In order to evaluate the possibility of kinetic self-sorting, we investigated reaction possibilities diverging from the two radicals (Scheme 4). Radical **B** has to overcome a relatively

Scheme 4. Calculated Gibbs Free Energy Surface for the Sn-Radical-Mediated Transformation of Biphenyl Phenyl Alkyne at 110°C[a]



[a]Energies are in kcal/mol relative to the isolated alkyne and Me_3Sn radical.

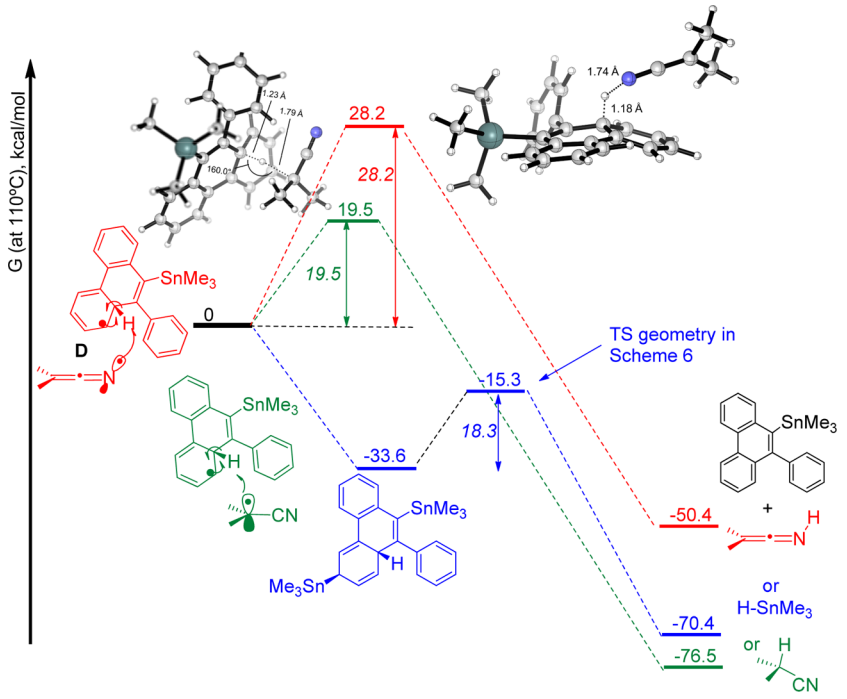
high barrier of ~17 kcal/mol to reach the 5-*exo* cyclization product **C**. The absolute value for this barrier is within 1 kcal/mol for the calculated barriers for the two routes (β-scission and 1,2-Sn shift) that convert this radical into the productive radical **A**. Lack of products derived from this path in the experimental work provides a much needed benchmark for theory, suggesting that the computational analysis either overestimates the barrier for **B** → **A** conversion or underestimates the barrier for the cyclization of **B**.

In contrast, the radical **A** was found to have a much lower "escape route" via the relatively low 8.2 kcal/mol activation barrier for the 6-*endo* cyclization. The cyclic radical **D** formed in the latter step is ~7 kcal/mol more stable than its vinyl radical precursor and ~10 kcal/mol more stable than the two reactants (Sn-radical and alkyne).

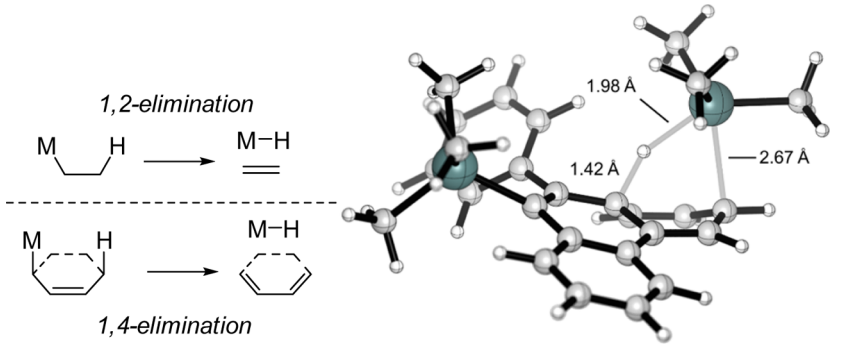
Routes to the Final Hydrogen Loss: The Key Oxidizing Step. There are two main routes for the oxidative (the formal

DOI: 10.1021/acs.joc.5b01014
J. Org. Chem. XXXX, XXX, XXX−XXX

Scheme 5. Mechanistic Possibilities for Aromatization of Polycyclic Radical D



Scheme 6. Left: Comparison between 1,2 and 1,4-Eliminations and Right: TS Geometry for Concerted Elimination of Bu_3SnH



loss of H atom) aromatization of 6-*endo* radical **D** into the final product. The direct H-abstraction at the relatively weak C−H bond at the ring junction is a straightforward one-step approach, and we have considered several possible routes for the final H atom abstraction mediated by the radicals present in the reaction mixture (Scheme 5). As the first step, we located a TS for C−H abstraction by the carbon-centered radical derived from AIBN (Scheme 5). Although this process is highly exergonic (ΔG = −76.5 kcal/mol) and clearly irreversible, the 19.5 kcal/mol barrier is fairly high, with the absolute energy ∼5 kcal/mol higher than TS for the phenanthrene ring opening back to the acyclic vinyl species.

Considering the possible role of steric hindrance in the barrier for this H-abstraction, we investigated reaction at the nitrogen atom of the α-CN-radicals derived from AIBN. Not only do such radicals have significant radical density at the nitrogen, the nitrogen atom has no other substituents, and its approach to the targeted C−H bond is not hindered. Indeed, we were able to find the respective TS. However, the process is ∼25 kcal/mol less exergonic (ΔG = −50.4), and the activation barrier for this step is ∼9 kcal/mol higher ($\Delta G^{\ddagger}$ = 28.2 kcal/mol), in a good agreement with the known correlation between the thermodynamics and kinetics of radical reactions.[14] The relatively low efficiency of these reactions is consistent with the experimental findings that reaction needs ∼2 equiv of such radicals per molecule of product in order to proceed to completion.

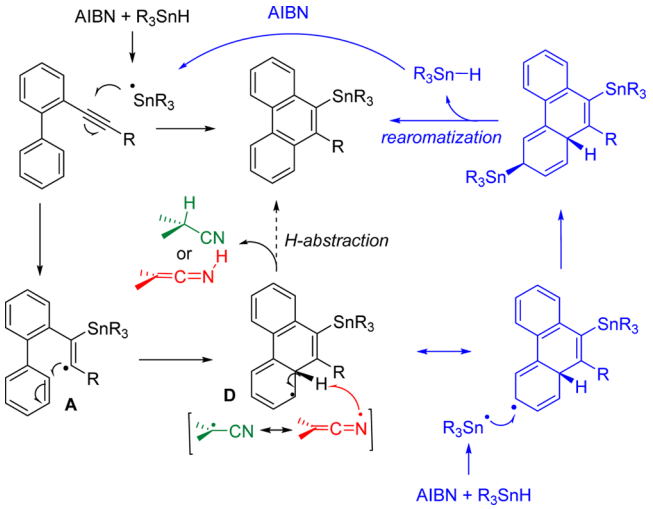
Finally, we investigated the possibility of H-abstraction from **D** by another $SnBu_3$ radical. The calculated TS energy was surprisingly low even considering the relatively high exergonicity (∼70 kcal/mol) of this process. Furthermore, the TS energy was negative and was located ∼15 kcal/mol lower than the reactants. A negative barrier in a chemical reaction generally suggests precomplexation between the reactants and, indeed, the further computational analysis located an additional minimum corresponding to the coupling product between SnR_3 and the cyclic radicals. The TS for the transformation of this intermediate to the final product corresponds to 1,4-elimination of Bu_3SnH via a concerted retro $[4\pi_s + 2\sigma_s]$ path (Scheme 6). Such 1,4-eliminations are known but much more rare[15] than 1,2-elimination of metal-hydrides.[16] Aromatization energy is likely to be important in the assisting this process in the present system.

DOI: 10.1021/acs.joc.5b01014
J. Org. Chem. XXXX, XXX, XXX−XXX

From the kinetic point of view, formation of Bu_3SnH is significant because it terminates the radical chain, accounting for the very low conversions in the absence of sufficient excess of AIBN. In this scenario, Bu_3Sn radical serves as a primary oxidant that is directly involved in the aromatization/oxidation step, whereas AIBN plays a secondary role by converting Bu_3SnH to Bu_3Sn radical and restarting the radical chain process.

The new radical route to phenanthrenes starts with the regioselective Bu_3Sn radical attack at the alkyne and formation of vinyl radical intermediate **A** from substrate **1a** (Scheme 7).

Scheme 7. Proposed Mechanism for Radical Cyclization



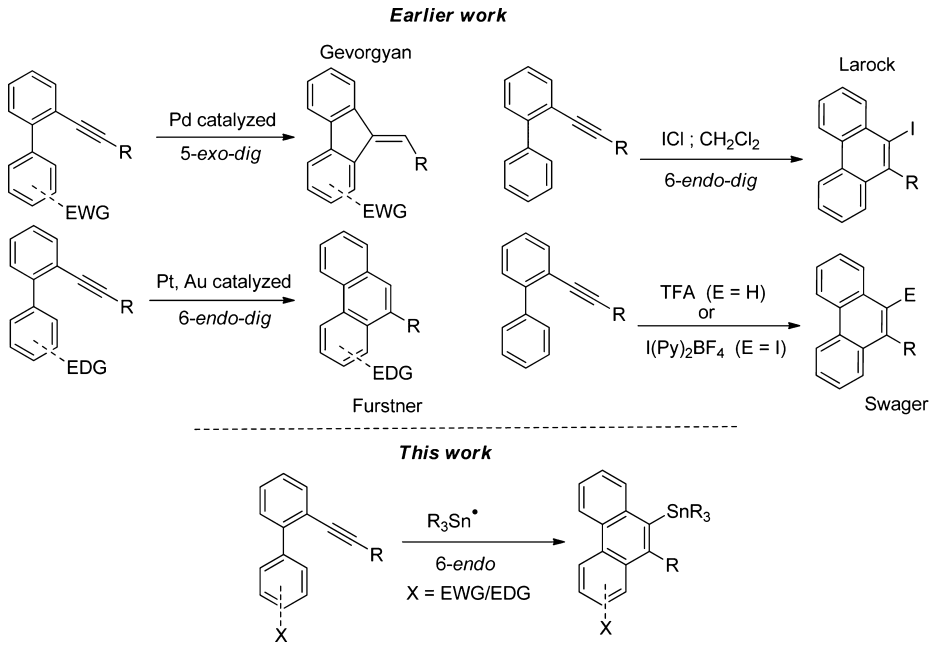
The vinyl radical **A** attacks π-system of the neighboring phenyl group via 6-*endo* cyclization to form the cyclic radical intermediate **D**. A second Bu_3Sn radical assists in the removal of hydrogen from C−H bond from intermediate **D**, which leads to the formation of the desired product phenanthrene **2a**.

Synthetic Applications. Phenanthrenes are an important class of polycyclic aromatic compounds and appear in many natural products[17] and biologically active molecules with antimicrobial,[18] anticancer,[19] and anti-HIV activities.[20] Moreover, phenanthrene is an important structural motif in materials science[21] due to its optical and electronic properties. Consequently, in the past two decades, extensive efforts have been focused on the development of new protocols for the construction of the phenanthrenes (Scheme 8).[22]

In particular, electrophile-assisted[23] and transition-metal-catalyzed reactions of 2-(arylethynyl)biphenyl derivatives represent a frequently utilized atom-economical strategy for the preparation of such compounds.[24] Swager and co-workers reported several acid- and electrophile-promoted cyclizations for the preparation of extended fused polycyclic aromatics.[25] Larock group reported the electrophile-assisted cyclization of 2-(arylethynyl)biphenyls with ICl, NBS, or arylsulfenyl chloride for the synthesis of phenanthrene derivatives.[26] More recently, several metal-catalyzed (Fe, In, Au, Pt, Pd) protocols have emerged.[27] In earlier works, the presence of EDG and EWG on the bottom ring of the biphenyl system has been shown to affect the regioselectivity of intramolecular hydroarylation. As reported by Gevorgyan, *o*-alkynylated biphenyls containing electron-withdrawing substituents undergo 5-*exo*-dig cyclization via Pd-catalyzed C−H activation pathway. In contrast, Fürstner found the 6-*endo*-dig preference for the transition-metal ($PtCl_2$, $InCl_3$, $GaCl_3$, AuCl) catalyzed cyclization of *o*-alkynylbiphenyls bearing an electron-rich aryl ring. The latter reaction proceeds via a Friedel−Crafts-type electrophilic aromatic substitution pathway following initial π-coordination of the metal to the alkyne unit.

Our work complements the literature methods by providing ready access to nucleophilic phenanthrenyl building blocks via a radical pathway. The polycyclic aromatic stannanes can be further elaborated using a variety of palladium-catalyzed processes, where they can be either used directly as nucleophilic components (i.e., in the Stille cross-coupling) in Pd-catalyzed cross-coupling or converted into the respective iodides that can

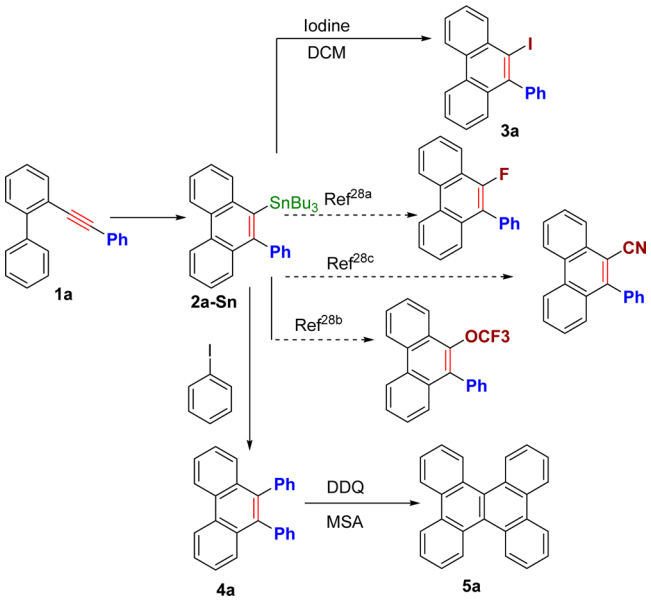
Scheme 8. Regioselective Alkyne Ring Closures of 2-(1-Alkynyl)-biphenyl Systems



DOI: 10.1021/acs.joc.5b01014
J. Org. Chem. XXXX, XXX, XXX−XXX

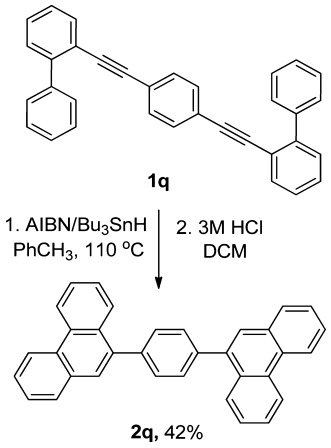
serve as electrophilic building blocks in Suzuki or Sonogashira cross-coupling. Furthermore, a variety of other interesting transformations are reported in the recent literature (Sn → CN, F, OCF_3, etc. as outlined in Scheme 9).

Scheme 9. Derivatization of Phenanthryl Stannanes[28]



Furthermore, the cascade can involve more than one biphenyl arylacetylene moiety as described in Scheme 10.

Scheme 10. Double Phenanthrene-Forming Cascade



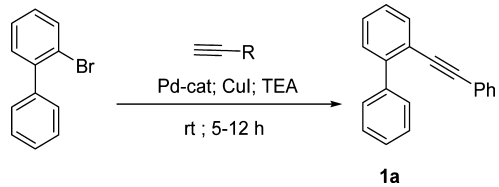
In summary, we have developed a new approach to substituted phenanthrene derivatives from 2-(arylethynyl)-biphenyls through a selective radical cascade which involves formation of the central ring of phenanthrene via regioselective vinyl radical formation followed by a 6-*endo* cyclization. Subsequent removal of hydrogen atom aromatizes the intermediate products and furnishes the final phenanthrenes in high yields. This radical cyclization opens a new avenue for the preparation of substituted polyaromatics. Future work will include expansion of this radical cascade toward the preparation of larger conjugated molecules and materials.

EXPERIMENTAL SECTION

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, toluene, tetrahydrofuran, and hexane were dried with a dry solvent system before use. Dichloromethane was dried over CaH_2 before use. Reagents were purchased from commercial sources and used without purification, unless otherwise stated. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) on 0.25 mm silica gel plates (60f-254) using UV light as visualizing agent. Time-of-flight mass spectrometer used for the analysis of HRMS. NMR spectra were recorded on a 400 and 600 MHz NMR spectrometer. Column chromatography was performed using Kieselgel 60 (70−230 mesh) or Kieselgel 60 (230−400 mesh). Preparative thin-layer chromatography (PTLC) separations were carried out on 0.25 or 0.55 mm silica gel plates (60F-254) in ethyl acetate/hexanes system.

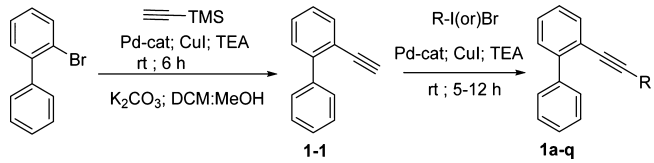
Procedure for NMR experiments to determine conversion rate and yields: The 8.8 ppm peak in H NMR spectra characteristic for the phenanthrene product and characteristic peak at 7.7 ppm for the starting material were compared with the peaks of triphenyl methane as internal standard. We also monitored C NMR data to confirm starting material consumption from the disappearance of alkyne carbon peaks. H NMR integration used to quantify reaction conversions and yields by using the peak at 8.8 characteristic for the phenanthrene products. We used triphenyl methane as standard.

Synthetic Scheme (A1) for the Preparation of 2-(Phenylethynyl)-1,1′-biphenyl (1a).



Procedure for Synthesis of 2-(Phenylethynyl)-1,1′-biphenyl ***1a****.* 2-Bromo-1,1′-biphenyl (1.00 g, 5.43 mmol) was added in one portion to a solution of CuI (0.10 g, 10 mol %) in Et_3N (30 mL) and degassed with nitrogen for 15 min at 23 °C. $PdCl_2(PPh_3)_2$ (0.32 g, 5 mol %) was added to the mixture and was stirred for 15 min before being treated with ethynylbenzene (0.63 g, 6.2 mmol) dropwise. The resulting solution was stirred at room temperature for 12 h and then filtered through a Celite pad, concentrated, and eluted (3% ethyl acetate/hexanes mixture used as eluent) through a silica column to give the desired 2-(phenylethynyl)-1,1′-biphenyl (**1a**) (0.94 g, 3.6 mmol, 86%).

Synthetic Scheme (A2) for the Preparation of 2-(Arylethynyl)-1,1′-biphenyls 1a−q.



General Procedure. 2-bromo-1,1′-biphenyl (1.7 g, 7.2 mmol), $Pd(PPh_3)_4$ (0.51 g, 0.44 mmol), and CuI (0.084 g, 0.44 mmol) were charged into a round flask and pumped under vacuo. Triethylamine (50 mL) was added into the flask. The mixture was stirred at rt, and trimethylsilylacetylene (1.2 mL, 8.7 mmol) was added dropwise to the mixture. The resulting mixture was stirred at rt for 10−14 h. The resulting material was passed through a short Celite bed with EtOAc:Hexane (1:1 ; 50 mL) and then washed with sat. NH_4Cl (50 mL), H_2O (50 mL × 2), and brine (50 mL). After the material was dried over Na_2SO_4, the solvent was removed by evaporation. The resulting material was dissolved in a mixture of DCM (20 mL) and MeOH (20 mL). K_2CO_3 (2.0 g, 14.6 mol) was added to the mixture and then stirred at rt for 5−6 h. The solid material was removed by filtration. The filtrate was concentrated by evaporation. The resulting crude material was purified with SiO_2 column chromatography (5%

DOI: 10.1021/acs.joc.5b01014
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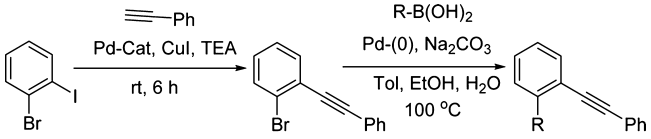
ethyl acetate/hexanes mixture used as eluent) to afford a desired product **1n−1o**.

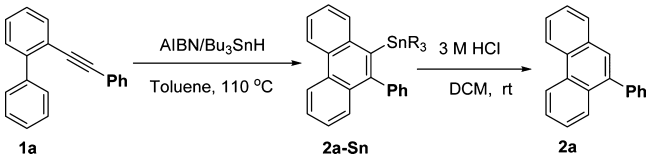
Synthetic Scheme (A3) for the Preparation of 2-(Arylethynyl)-1,1′-biphenyls 1n and 1o.



R = 4-Me-C_6H_5; 4-F-C_6H_5

To a solution of Na_2CO_3 (3.26 g, 31.1 mmol) in toluene (45 mL), ethanol (15 mL), and water (15 mL) was added 1-bromo-2-(phenylethynyl)benzene (2.0 g, 7.8 mmol) at room temperature, and the solution was degassed with nitrogen. To this mixture was added 4-methyl phenylboronic acid (1.37 g, 10.1 mmol) and $Pd(PPh_3)_4$ (0.63 g, 7 mol %), and the resulting mixture was heated to 100 °C for 10 h. After completion of the reaction, the solution was cooled to room temperature and washed with water, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate, washed with brine solution, dried over $MgSO_4$, and concentrated. The residues were eluted (5−10% ethyl acetate/hexanes mixture used as eluent) through a silica column to give the desired compound (**1n−o**).

General Procedure Synthetic Scheme (A4) for the Synthesis of 9-Phenylphenanthrenes (2a−2p).



A solution of 0.10 g (0.39 mmol) of 2-(phenylethynyl)-1,1′-biphenyl **1a** in 10 mL of toluene (0.04 M solution) was fitted with a condenser and degassed by purging with argon gas. AIBN (0.064 g, 0.39 mmol) and Bu_3SnH (0.137 g, 0.47 mmol) were dissolved separately in dry toluene and added slowly (flow rate 1 mL/h) to the reaction mixture by using a syringe pump at 110 °C. The progress of reaction was monitored by TLC. After consumption of the starting material, the reaction mixture was allowed to cool down to room temperature and filtered through a small Celite bed. Solvent was removed under reduced pressure. The crude reaction mixture was dissolved in 20 mL DCM. Aq. HCl (3 M) (15 mL) was added to above mixture and stirred for 4 h. The reaction mixture was extracted with DCM (30 mL). The extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was eluted through a silica column to afford compound purified by column chromatography over silica gel (1% ethyl acetate/hexanes mixture used as eluent), which yielded 9-phenylphenanthrene **2a** (0.090 g, 0.33 mmol, 90%).

*2-(Phenylethynyl)-1,1′-biphenyl (**1a**).* NMR data for this compound are identical to those reported in the literature.[22d] Yield: 0.94 g (87%). Compound **1a** prepared using synthetic Scheme A1. 2% ethyl acetate/hexanes mixture used as eluent. Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72−7.67 (m, 3H), 7.50−7.30 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.9, 140.5, 132.8, 131.3 (2 × CH), 129.4, 129.37 (2 × CH), 128.5, 128.2 (2 × CH), 128.1, 127.8 (2 × CH), 127.4, 127.0, 123.4, 121.5, 92.2, 89.4.

*2-(p-Tolylethynyl)-1,1′-biphenyl (**1b**).* NMR data for this compound are identical to those reported in the literature.[22d] Yield: 0.129 g (86%). Compound **1b** prepared using synthetic Scheme A2. 1% ethyl acetate/hexanes mixture used as eluent. Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69−7.63 (m, 3H), 7.48−7.31 (m, 6H), 7.23 (d, J = 8 Hz, 2H), 7.10 (d, J = 8 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.7, 140.5, 138.2, 132.7, 131.2 (2 × CH), 129.4 (2 × CH), 129.3, 128.9 (2 × CH), 128.3, 127.8 (2 × CH), 127.3, 127.0, 121.7, 120.3, 92.4, 88.7, 21.5.

*2-((4-Fluorophenyl)ethynyl)-1,1′-biphenyl (**1c**).*[29] Yield: 0.119 g (78%). 12% ethyl acetate/hexanes mixture used as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.65 (m, 3H), 7.47−7.31 (m, 8H), 7.03−6.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.3 (d, J_f = 247.41 Hz), 143.8, 140.5, 133.2, 133.1, 132.7 (2 × CH), 129.4, 129.3 (2 × CH), 128.5, 127.8, 127.4, 127.8, 127.4, 127.0, 120.4 (d, J_f = 190.29 Hz), 115.6, 115.4, 90.1 (d, J_f = 206.18 Hz).

*4-([1,1′-Biphenyl]-2-ylethynyl)benzonitrile (**1d**).*[22d] Yield: 0.113 g (72%). Synthetic Scheme A2. 8% ethyl acetate/hexanes mixture used as eluent. Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, J = 7.68 Hz, 1H), 7.64−7.62 (m, 2H), 7.56 (d, J = 10.86 Hz, 2H), 7.48−7.41 (m, 5H), 7.38−7.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.5, 140.3, 133.0, 132.0 (2 × CH), 131.8 (2 × CH), 129.6, 129.4, 129.4 (2 × CH), 128.4, 128.0, 127.7, 127.2 (2 × qC), 120.6, 118.6, 111.2, 93.9, 90.5. HRMS calcd for $C_{21}H_{13}N$: 279.1048, found $[M]^+$: 279.1056.

*2-((4-(Trifluoromethyl)phenyl)ethynyl)-1,1′-biphenyl (**1e**).* NMR data for this compound are identical to those reported in the literature.[22d] Yield: 0.145 g (80%). Synthetic Scheme A4. 10% ethyl acetate/hexanes mixture used as eluent. Pale brown liquid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67−7.64 (m, 3H), 7.54 (d, J = 8.3 Hz, 2H), 7.48−7.40 (m, 7H), 7.38−7.35 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.3, 140.4, 132.9, 131.5, 129.8, 129.5, 129.3, 129.1, 127.9, 127.6, 127.2, 127.1, 125.2, 125.18, 125.15, 125.1, 124.8, 123.0, 120.9, 91.8, 90.7; HRMS calcd for $C_{21}H_{13}F_3$: 322.0969, found $[M]^+$: 322.0983.

*1-([1,1′-Biphenyl]-2-ylethynyl)naphthalene (**1f**).* NMR data for this compound are identical to those reported in the literature.[22d] 5% ethyl acetate/hexanes mixture used as eluent. Yield: 0.157 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ. 7.94 (d, J = 8 Hz, 1H), 7.87−7.82 (m, 3H), 7.79−7.76 (m, 2H) 7.68 (dd, J = 1.12 Hz, 6 Hz, 1H), 7.59−7.42 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.1, 140. 9, 133.1, 133.0, 132.9, 130.1, 129.5, 129.4 (2 × CH), 128.5, 128.5, 128.1 (2 × CH), 128.0, 127.4, 127.1, 126.5, 126.3, 126.2, 125.1, 121.9, 121.0, 94.1, 90.5.

*2-(Hex-1-yn-1-yl)-1,1′-biphenyl (**1g**).* NMR data for this compound are identical to those reported in the literature.[26] 2% ethyl acetate/hexanes mixture used as eluent. Yield: 0.118 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61−7.59 (m, 2H), 7.54−7.52 (m, 1H), 7.44−7.27 (m, 6H), 2.31 (t, J = 6.88 Hz, 2H), 1.48−1.30 (m, 4H), 0.88 (t, J = 7.32 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.6, 140.8, 132.9, 129.3, 129.2 (2 × CH), 127.7 (2 × CH), 127.6, 127.1, 126.8, 122.3, 93.4, 80.0, 30.4, 21.8, 19.1, 13.6. HRMS calcd for $C_{18}H_{18}$: 234.1409, found $[M]^+$: 234.1407.

*2-((4-Methoxyphenyl)ethynyl)-1,1′-biphenyl (**1h**).* NMR data for this compound are identical to those reported in the literature.[22d] Yield: 0.144 g (90%) Synthetic Scheme A2. 8% ethyl acetate/hexanes mixture used as eluent. Clear oil (with a very slight hint of yellow). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69−7.68 (m, 2H), 7.65−7.63 (m, 1H), 7.48−7.37 (m, 5H), 7.33 (t of d, J_1 = 7.5 Hz, J_2 = 1.44 Hz, 1H), 7.29−7.27 (m, 2H), 6.83−6.82 (m, 2H), 3.80 (s, 3H). 13C NMR(100 MHz, $CDCl_3$): 159.5, 143.6, 140.7, 132.8 (2 × CH), 132.6, 129.4, 129.39, 128.1, 127.8 (2 × CH), 127.4, 127.0 (2 × qC), 121.9, 115.6, 113.9 (2 × CH), 92.2, 88.0, 55.2.

*2-([1,1′-Biphenyl]-2-ylethynyl)thiophene(**1i**).* NMR data for this compound are identical to those reported in the literature.[26] Yield: 0.111 g (76%). Synthetic Scheme A2. 6% ethyl acetate/hexanes mixture used as eluent. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67−7−66 (m, 2H), 7.64 (d, J = 7.56 Hz, 1H), 7.49−7.44 (m, 3H), 7.43−7.39 (m, 2H), 7.34 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz 1H), 7.24 (dd, J_1 = 5.2 Hz, J_2 = 1.0 Hz 1H), 7.11 (dd, J_1= 3.5 Hz, J_2 = 1 Hz, 1H), 6.97−6.96 (m, 1H). ^{13}C NMR(100 MHz, $CDCl_3$): 143.7, 140.4, 132.5, 131.5, 129.5, 129.3 (2 × CH), 128.7, 128.0 (2 × CH), 127.5, 127.2, 127.1, 127.0, 123.5, 121.3, 93.2, 85.6. HRMS calcd for $C_{18}H_{12}S$: 260.0660, found $[M]^+$: 260.0684.

*2-(2-((4-Methoxyphenyl)ethynyl)-4-methylphenyl)benzofuran (**1j**).*[33] 10% ethyl acetate/hexanes mixture used as eluent. Yield: 0.109 g (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.12 Hz, 1H), 7.75 (s, 1H), 7.64 (d, J = 7.44 Hz, 1H), 7.58−7.55 (m, 3H), 7.50 (s, 1H), 7.34−7.30 (m, 1H), 7.28−7.24 (m, 2H), 6.97−6.94 (m, 2H), 3.86 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.8, 154.2, 154.1, 137.7, 134.1, 132.9 (2 × CH), 129.4, 129.3, 128.5, 126.5, 124.3, 122.7, 121.1, 119.7, 115.4, 114.1 (2 × CH), 110.9, 105.0, 94.2,

DOI: 10.1021/acs.joc.5b01014
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88.2, 55.3, 20.9. HRMS calcd for $C_{24}H_{18}O_2$: 338.1307, found $[M]^+$: 338.1305.

*4-([1,1′-Biphenyl]-2-ylethynyl)pyridine (**1k**).* 15% ethyl acetate/hexanes mixture used as eluent. Yield: 0.100 g (70%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.54 (s, 2H), 7.66 (d, J = 7.62 Hz, 1H), 7.63 (d, J = 7.98 Hz, 2H) 7.48−7.41(m, 5H), 7.36−7.33 (m, 1H), 7.15 (d, J = 5.64 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): 149.5(2 × C), 144.4, 140.0, 133.0, 131.3, 129.4, 129.4, 129.2 (2 × CH), 127.8 (3 × CH), 127.6, 127.0, 125.1, 120.2, 93.9, 89.2. HRMS calcd for $C_{19}H_{13}N$: 255.1048, found $[M]^+$: 255.1036.

*5-([1,1′-Biphenyl]-2-ylethynyl)benzo[d][1,3]dioxole (**1l**).* Yield: 0.137 g (82%). Synthetic Scheme A1. 9% ethyl acetate/hexanes mixture used as eluent. Pale orange semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69−7.63 (m, 3H), 7.51−7.33 (m, 6H), 6.88 (dd, J = 1.5 Hz, 1.5 Hz, 1H), 6.79−6.75 (m, 2H), 5.98 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.9, 147.4, 143.8, 140.71, 132.7, 129.53 (2 × CH), 129.48, 128.4 (2 × CH), 128.0, 127.6, 127.1, 126.1, 121.8, 116.8, 111.4, 108.5, 101.3, 92.3, 88.0; HRMS calcd for $C_{21}H_{14}O_2$: 298.0994, found $[M]^+$: 298.1002.

*2-([1,1′-Biphenyl]-2-ylethynyl)benzo[b]thiophene (**1m**).*[40] Yield: 0.136 g (78%). Synthetic Scheme A1, 10% ethyl acetate/hexanes mixture used as eluent. Orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.77−7.68 (m, 5 H), 7.54−7.43 (m, 5 H), 7.39−7.35 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 140.3, 140.3, 139.1, 132.8 (2 × CH), 129.6, 129.3 (2 × CH), 129.1, 128.3, 128.1, 127.7, 127.1, 125.3, 124.7, 123.8, 123.5, 122.0, 121.0, 95.1, 85.9.; HRMS calcd for $C_{22}H_{14}S$: 310.0816, found $[M]^+$: 310.0828

*4′-Methyl-2-(phenylethynyl)-1,1′-biphenyl (**1n**).* 3% ethyl acetate/hexanes mixture used as eluent. Yield: 0.140 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, J = 1 Hz, 6.56 Hz, 1H), 7.67 (d, J = 8.08 Hz, 2H) 7.55−7.33 (m, 10H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.7, 137.6, 137.1, 132.9, 131.3 (2 × CH), 129.4, 129.2 (2 × CH), 128.6 (2 × CH), 128.5, 128.2 (2 × CH), 128.0, 126.7, 123.5, 121.4, 92.0, 89.5, 21.2. HRMS calcd for $C_{21}H_{16}$: 268.1252, found $[M]^+$: 268.1274.

*4′-Fluoro-2-(phenylethynyl)-1,1′-biphenyl (**1o**).* 12% ethyl acetate/hexanes mixture used as eluent. Yield: 0.210 g (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.63 (m, 3H), 7.42 (d, J = 8.68 Hz, 2H), 7.38−7.30 (m, 6H), 7.16 (t, J = 8.76 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.38 (d, J_f = 245.34 Hz), 142.77, 136.5, 132.9, 131.3 (2 × CH), 131.0, 130.9, 129.3, 128.5, 128.3 (2 × CH), 128.2, 127.1, 123.2, 121.5, 114.7 (d, J_f = 21.25 Hz), 92.3, 89.0. Peaks for several chemically nonequivalent carbons overlap with each other. HRMS calcd for $C_{20}H_{13}F$: 272.1001, found $[M]^+$: 272.1011.

*1-(4-([1,1′-Biphenyl]-2-ylethynyl)phenyl)ethan-1-one (**1p**).* 4% ethyl acetate/hexanes mixture used as eluent. Yield: 0.141 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (m, 2H), 7.66−7.64 (m, 3H), 7.47−7.36 (m, 8H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 197.3, 144.3, 140.4, 137.9, 136.0, 132.9, 131.4 (2 × CH), 129.5, 129.4 (2 × CH), 129.1, 128.4 (2 × CH), 128.2, 127.9, 127.6, 127.1, 121.1, 92.8, 91.4, 26.6. HRMS calcd for $C_{22}H_{16}O$: 296.1201, found $[M]^+$: 296.1206.

*1,4-Bis([1,1′-biphenyl]-2-ylethynyl)benzene (**1q**).* 10% ethyl acetate/hexanes mixture used as eluent. Yield: 0.230 g (64%). NMR data for this compound are identical to those reported in the literature.[35] Pale yellow thick syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72−7.71 (m, 3H), 7.69−7.43 (m, 5H), 7.39−7.30 (m, 1H), 7.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.9, 140.4, 132.8,132.1 (2 × CH), 129.4 (2 × CH), 129.3, 128.6 (2 × CH), 127.8, 127.4, 127.0, 123.0, 121.3, 91.9, 91.2. HRMS calcd for $C_{34}H_{22}$: 430.1722, found $[M]^+$: 430.1746.

*9-Phenylphenanthrene (**2a**).* (NMR data for this compound are identical to those reported in the literature.)[30] 1% ethyl acetate/hexanes mixture used as eluent. Yield 0.090 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81−8.79 (m, 2H), 7.93−7.90 (m, 2H), 7.71−7.55 (m, 4H), 7.53−7.46 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 140.7, 138.7, 131.5, 131.1, 130.6, 130.0 (2 × CH), 129.9, 128.6, 128.3 (2 × CH), 127.5, 127.3, 126.9, 126.8, 126.5, 126.47, 126.42, 122.9, 122.5.

*Tributyl(10-phenylphenanthren-9-yl)stannane (**2a−Sn**).* This compound was prepared using the same procedure as shown in general procedure A4. Hexanes was used as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89−8.81 (m, 2H), 8.07 (d, J = 7.98 Hz, 1H), 7.71−7.62 (m, 2H), 7.50−7.34(m, 3H), 7.33−7.27(m, 5H), 1.38−1.35 (m, 6H), 1.24−1.21 (m, 6H), 0.82−0.73 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): 148.1, 143.5, 141.8, 136.7, 131.8, 131.0, 130.8, 130.5, 129.8, 128.3, 127.4, 127.3, 126.3, 126.2, 125.8, 122.9, 122.3, 29.07, 27.1, 13.6, 11.9. Peaks for several chemically nonequivalent carbons overlap with each other.

*9-(p-Tolyl)phenanthrene (**2b**).* NMR data for this compound are identical to those reported in the literature.[26c] 2% ethyl acetate/hexanes mixture used as eluent. Yield: 0.049 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (dd, J = 0.44 Hz, 8.26 Hz,1H), 8. 73 (d, J = 8.16 Hz, 1H), 7.95 (d, J = 8.24 Hz, 1H), 7.89 (dd, J = 0.6 Hz, 7.48 Hz, 1H), 7.69−7.59 (m, 4H), 7.56−7.51 (m, 1H), 7.45 (d, J = 7.92 Hz, 2H), 7.34−7.32 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): 138.8, 137.9, 137.1, 131.6, 131.3, 130.6, 129.9, 129.0 (2 × CH), 128.6, 127.4, 127.0, 126.8, 126.5, 126.4, 126.4, 122.9, 122.5, 21.3.

*9-(4-Fluorophenyl)phenanthrene (**2c**).* NMR data for this compound are identical to those reported in the literature.[26c] 12% ethyl acetate/hexanes mixture used as eluent. Yield: 0.068 g (85%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.78 (d, J = 8.22 Hz, 1H), 8.73 (d, J = 8.16 Hz, 1H), 7.90 (d, J = 7.74 Hz, 1H), 7.86 (d, J = 7.92 Hz, 1H), 7.70−7.62 (m, 4H), 7.57−7.50 (m, 3H), 7.21 (t, J = 8.52 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): 162.31 (d, J_f = 245.01 Hz), 137.65, 136.65, 131.60, 131.55, 131.42, 131.08, 130.62, 129.96, 128.62, 127.64, 126.90, 126.69, 126.65, 126.57, 126.52, 122.95, 122.53, 115.29, 115.15.

*4-(Phenanthren-9-yl)benzonitrile (**2d**).* NMR data for this compound are identical to those reported in the literature.[31] Yield: 0.032 g (64%). Synthetic Scheme A4. 9% ethyl acetate/hexanes mixture used as eluent. White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.80 (d, J = 8.28 Hz, 1H), 8.74 (d, J = 8.34 Hz, 1H), 7.91 (d, J = 7.86 Hz, 1H), 7.82 (d, J = 8.10 Hz, 2H), 7.78 (d, J = 8.22 Hz, 1H), 7.73−7.70 (m, 2H), 7.68−7.63 (m, 4H), 7.57 (t, J = 7.56 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): 145.8, 136.8, 132.2 (2 × CH), 131.2, 130.8 (2 × CH), 130.7, 130.3, 130.2, 128.9, 127.9, 127.3, 127.2, 126.9, 126.8, 126.2, 123.2, 122.6, 118.9, 111.3. HMRS-DART calcd for $C_{21}H_{13}N$ +NH_4: 297.1392, found $[M + NH_4]^+$: 297.1378.

*9-(4-(Trifluoromethyl)phenyl)phenanthrene(**2e**).* NMR data for this compound are identical to those reported in the literature.[32] 10 % ethyl acetate/hexanes mixture used as eluent. Yield: 0. 080 g (80%). White solid (m.p.: 162−163 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.78 (dd, J = 8.3 Hz, 26.6 Hz, 2H), 7.92 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.73−7.65 (m, 6H), 7.58−7.56 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 137.3, 131.3, 130.7, 130.6, 130.4, 130.2, 129.9, 129.8, 128.2, 127.8, 127.07, 127.05, 126.8, 126.6, 126.5, 125.33, 125.30, 123.1, 122.6; CF_3 carbons are merging with other peaks.

*9-(Naphthalen-1-yl)phenanthrene (**2f**).* NMR data for this compound are identical to those reported in the literature.[26] 4% ethyl acetate/hexanes mixture used as eluent. Yield: 0. 067 g (84%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.84 (d, J = 8.4 Hz, 1H), 8.82 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.16 Hz, 1H), 7.99 (d, J = 8.04 Hz, 1H), 7.92 (d, J = 7.74 Hz, 1H), 7.81 (s, 1H), 7.75−7.73 (m, 1H), 7.68−7.63 (m, 3H), 7.60−7.59 (m, 1H), 7.51−7.46 (m, 3H), 7.43−7.40 (m, 1H), 7.31−7.29 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): 138.4, 137.0, 133.5, 132.9, 132.1, 131.5, 130.2, 130.2, 128.6, 128.4, 128.1, 128.0, 127.8, 127.4, 126.8, 126.7, 126.6, 126.5, 126.4, 126.0, 125.8, 125.4, 122.7, 122.6.

*9-(4-Butylphenyl)phenanthrene (**2g**).* NMR data for this compound are identical to those reported in the literature.[33] 1% ethyl acetate/hexanes mixture used as eluent. Yield: 0.075 g (75%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.75−8.73 (m, 1H), 8.66 (d, J = 8.04 Hz, 1H), 8.13−8.11 (m, 1H), 7.83−7.82 (m, 1H), 7.67−7.56 (m, 5H), 3.12 (t, J = 7.8 Hz, 2H), 1.82−1.78 (m, 2H), 1.53−1.50 (m, 2H), 1.00 (t, J = 7.32 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): 136.9, 131.9, 131.3, 130.7, 129.6, 128.0, 126.5, 126.4, 126.0, 125.9, 125.8, 124.5, 123.2, 122.1, 33.2, 32.4, 22.9, 14.0.

*9-(4-Methoxyphenyl)phenanthrene (**2h**).* NMR data for this compound are identical to those reported in the literature.[26] 6% ethyl acetate/hexanes mixture used as eluent. Yield: 0.80 g (80%). White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.78 (d, J = 2.82 Hz, 1H)

DOI: 10.1021/acs.joc.5b01014
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8.73 (d, J = 8.16 Hz, 1H), 7.95 (d, J = 8.28 Hz, 1H), 7.89 (d, J = 7.62 Hz, 1H), 7.69−7.65 (m, 3H), 7.62 (t, J = 7.44 Hz, 1H), 7.55 (t, J = 7.29 Hz, 1H), 7.50−7.47 (m, 2H), 7.08−7.06 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): 159.0, 138.4, 133.2, 131.7, 131.4, 131.1 (2 × CH), 130.7, 129.9, 128.6, 127.4, 126.9, 126.8, 126.5, 126.4, 122.9, 122.5, 113.8. 55.4. Chemically nonequivalent carbons are merging with other peaks. LRMS-EI calcd for $C_{21}H_{16}O$: 284.12, found $[M]^+$: 282.26.

*2-(Phenanthren-9-yl)thiophene (**2i**).* NMR data for this compound are identical to those reported in the literature.[34] 5% ethyl acetate/hexanes mixture used as eluent. Yield: 0.074 g (74%). Synthetic Scheme A4. White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.78 (d, J = 8.2 Hz, 1H), 8.71 (d, J = 8.3 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.86 (s, 1H), 7.69 (q, J = 7.5 Hz 1H), 7.64−7.59 (m, 2H) 7.46 (d, J = 5.0 Hz, 1H) 7.30 (d, J = 3.3 Hz, 1H) 7.23−7.22 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): 141.7, 131.3, 131.1, 131.0, 130.7, 130.2, 129.1, 128.8, 127.6, 127.3, 127.1, 127.0, 126.8, 126.7, 126.6, 125.6, 122.9, 122.6. (solvent (DCM) peak at 53.4).

*6-(4-Methoxyphenyl)-3-methylnaphtho[1,2-b]benzofuran (**2j**).* NMR data for this compound are identical to those reported in the literature.[35] 15% ethyl acetate/hexanes mixture used as eluent. Yield: 0.035 g (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.40 (m, 2H), 7.38−7.36 (m, 1H), 7.32−7.28 (m, 1H), 7.15−7.12 (m, 2H), 7.09 (s, 1H), 7.00−6.97 (m, 3H), 6.80 (t, J = 3.56 Hz, 2H), 3.86 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.2, 152.8, 143.6, 143.5, 142.2, 138.9, 131.3, 130.6 (2 × CH). 130.1, 130.1, 129.6, 128.1, 126.8, 125.9, 123.2, 121.5, 120.6, 115.9, 113.9 (2 × CH), 53.3, 21.6. Chemically nonequivalent carbons are merging with other peaks. HRMS-DART calcd for $C_{24}H_{18}O_2$ + H: 339.1385, found $[M + H]^+$:339.1387.

*4-(10-(Tributylstannyl)phenanthren-9-yl)pyridine(**2k**−**Sn**).* This compound prepared same procedure as general procedure synthetic Scheme A4. 10% ethyl acetate/hexanes mixture used as eluent. Yield: 0.173 g (81%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.79−8.75 (m, 4H), 8.07 (d, J = 7.98 Hz, 1H), 7.68 (t, J = 7.14 Hz,1H), 7.65−7.61(m, 2H), 7.44(t, J = 7.98 Hz, 1H) 7.34 (d, J = 5.76 Hz, 2H), 7.27 (d, J = 8.28 Hz, 1H), 1.38−1.35 (m, 6H), 1.24−1.21 (m, 6H), 0.82−0.73 (m, 15H). ^{13}C NMR (150 MHz, $CDCl_3$): 151.4, 149.8, 145.3, 141.7, 136.3, 130.9, 130.6, 130.5, 129.9, 126.7, 126.7, 126.5, 126.4, 126.4, 126.3, 123.0, 123.6, 29.0, 27.1, 13.5, 13.3. Peaks for several chemically nonequivalent carbons overlap with each other. The compound is not ionized under HRMS conditions.

*5-(Phenanthren-9-yl)benzo[d][1,3]dioxole (**2l**).* NMR data for this compound are identical to those reported in the literature.[26c,36] Yield: 0.082 g (82%). 5% ethyl acetate/hexanes mixture used as eluent.Pale orange solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.75 (dd, J = 8.3 Hz, 2.6 Hz, 2H), 7.96 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.68−7.65 (m, 3H), 7.63 (t, J = 15.5 Hz, 1H), 7.54 (t, J = 16.0 Hz, 1H), 7.04−6.96 (m, 3H), 6.07 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.5, 147.0, 138.3, 134.6, 131.5, 131.3, 130.6, 129.9, 128.6, 127.5, 126.88, 126.86, 126.6, 126.53, 126.5, 123.4, 122.9, 122.5, 110.7, 108.3, 101.2.

*2-(Phenanthren-9-yl)benzo[b]thiophene (**2m**).* NMR data for this compound are identical to those reported in the literature.[37] 8% ethyl acetate/hexanes mixture used as eluent. Yield: 0.038 g (76%). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (dd, J = 8.2 Hz, 15.4 Hz, 2H), 8.32 (d, J = 8.0 Hz, 1 H), 7.95−7.87 (m, 4 H), 7.71 (t, J = 7.1 Hz, 2 H), 7.66−7.59 (m, 2 H), 7.52 (s, 1H), 7.44−7.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.2, 140.3, 140.2, 131.2, 131.1, 130.9, 130.7, 130.4, 129.5, 128.9, 127.3, 127.1, 126.9, 126.87, 126.7, 124.5, 124.4, 124.3, 123.6, 123.0, 122.6, 122.2.

*2-Methyl-10-phenylphenanthrene (**2n**).* 2% ethyl acetate/hexanes mixture used as eluent. Yield: 0.046 g (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (t, J = 6.76 Hz, 2H), 7.88 (d, J = 7.8 Hz, 1H), 7.71−7.48 (m, 10H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 140.9, 138.5, 136.3, 131.2, 131.1, 131.0 (2 × CH), 130.0, 128.5, 128.4 (2 × CH), 128.1, 127.6, 127.2, 126.8 (2 × CH), 126.5, 126.4, 122.8, 122.3, 21.7; LRMS-EI calcd for $C_{21}H_{16}$: 268.12 found, $[M]^+$: 268.26. The compound is not ionized under HRMS conditions.

*2-Fluoro-10-phenylphenanthrene (**2o**).* 8% ethyl acetate/hexanes mixture used as eluent. Yield: 0.066 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77−8.73 (m, 1H), 8.65 (d, J = 8.16 Hz, 1H), 7.91 (d, J = 7.56 Hz, 1H), 7.74 (s, 1H), 7.71−7.39 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 161.3 (d, J_f = 244.14 Hz), 138.1, 132.7, 132.7, 131.0, 129.8 (2 × CH), 129.6, 128.7, 128.6, 128.5 (2 × CH), 127.6, 127.2, 126.9, 126.7, 125.2, 125.1, 115.3 (d, J_f = 23.6 Hz), 111.36 (d, J_f = 21.89 Hz). LRMS-EI calcd for $C_{20}H_{13}F$: 272.10, found $[M]^+$: 272.19. The compound is not ionized under HRMS conditions.

*1-(4-(Phenanthren-9-yl)phenyl)ethan-1-one (**2p**).* NMR data for this compound are identical to those reported in the literature.[38] Yield: 0. 064 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80−8.72 (m, 2H), 8.12 (dd, J = 8.52 Hz, 1.8 Hz, 2H), 7.91 (dd, J = 1.36 Hz, 7.72 Hz, 1H), 7.85 (dd, J = 0.92 Hz, 8.32 Hz, 1H), 7.69−7.60 (m, 6H), 7.57−7.55 (m, 1H), 2.71 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): 197.8, 145.8, 137.5, 136.1, 131.2, 130.62, 130.5, 130.3 (2 × CH), 130.1, 128.7, 128.4 (2 × CH), 127.6, 126.9 (2 × qC), 126.95 (2q C), 126.67 (2 × CH), 126.5, 26.7. LRMS-EI calcd for $C_{22}H_{16}O$: 296.12, found $[M]^+$: 296.26. The compound is not ionized under HRMS conditions.

*9-Iodo-10-phenylphenanthrene (**3a**).* NMR data for this compound are identical to those reported in the literature.[39] Hexanes mixture used as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, J = 8.32 Hz, 1H), 8.72−8.69 (m, 1H), 8.55−8.52 (m, 1H), 7.75−7.67 (m, 3H), 7.64−7.56 (m, 3H), 7.49−7.45 (m, 2H), 7.37−7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.3, 145.2, 134.6, 132.3, 132.2, 130.4, 130.1, 129.9 (2 × CH), 128.6, 128.4 (2 × CH), 128.0, 127.7, 127.4, 127.0, 126.9, 122.5, 122.5, 106.5. LRMS-EI calcd for $C_{20}H_{13}I$: 380.00, found $[M]^+$: 379.99.

*1,4-Bis(10-phenylphenanthren-9-yl)benzene (**2q**).* NMR data for this compound are identical to those reported in the literature.[40] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, J = 8.2 Hz, 1H), 8.86 (d, J = 8.08 Hz, 1H), 8.12 (d, J = 7.68 Hz, 1H), 7.96 (d, J = 6.44 Hz, 1H), 7.82 (s, 1H), 7.74−7.61 (m, 6H). This compound decomposes slowly.

*9,10-Diphenylphenanthrene (**4a**).* NMR data for this compound are identical to those reported in the literature.[41] ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.83 (d, J = 8.28 Hz, 2H), 7.71−7.68 (m, 2H), 7.60 (d, J = 8.22 Hz, 2H), 7.51 (t, J = 7.98 Hz, 2H), 7.28−7.18(m, 10H). ^{13}C NMR (150 MHz, $CDCl_3$): 139.5, 137.1, 131.8, 131.0 (3 × CH), 129.9, 127.8, 127.5 (2 × CH), 126.6, 126.4, 126.4, 122.5. Peaks for several chemically nonequivalent carbons overlap with each other.

*Dibenzochrysene (**5a**).* NMR data for this compound are identical to those reported in the literature.[42] 9,10-Diphenylphenanthrene (33 mg 0.1 mmol) was dissolved in dry dichloromethane (9 mL) and cooled to ∼0 °C. To this solution, methanesulfonic acid (1 mL) and solid DDQ (23 mg, 0.1 mmol) were added, and the resulting highly colored mixture was stirred. After 30 min, the resulting reaction mixture was quenched by pouring onto saturated aqueous $NaHCO_3$ (20 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 10 mL). Combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, and evaporated under vacuum to afford DBC, which was purified by filtration through a short pad of silica gel using 1:9 mixture of ethyl acetate and hexanes to afford pure dibenzochrysene. Yield: 80%, 1H NMR δ: 2.64 (s, 3H), 7.43 (d, 3H, J = 8.43 Hz, 1.4 Hz), 8.47 (s, 3H), 8.56 (d, 3H, J = 8.4 Hz); 13C NMR δ: 22.0, 123.6, 126.6, 127.5, 128.0, 128.9, 130.8, 136.0.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01014.

^{1}H NMR, ^{13}C NMR, NMR spectra for all of the prepared compounds (PDF)

Compound **3a** data and its crystal structure and computational details for all calculated structures(CIF)

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DOI: 10.1021/acs.joc.5b01014
J. Org. Chem. XXXX, XXX, XXX−XXX

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Science Foundation (CHE-1465142) for support of this research and to the Research Computing Center of the Florida State University for the allocation of computational resources.

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