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Platinum-Mediated Intramolecular Cyclization of Biphenyl Propargyl Alcohol: Highly Regioselective Synthesis of Phenanthrenes

2015年 2月

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I. Abstract

Polycyclic aromatic hydrocarbons have received attention, especially in materials science, because of their utility in photoelectronic devices such as field-effect transistors, light emitting diodes, and solar cells. Most of the group consist of phenanthrene molecules are commonly biologically active. A variety of approaches for the development of their backbone have been established. The synthesis of phenanthrene skeleton has important values as they generally offer selective and efficient routes to functionalized derivatives directly from simple substrates in fewer steps and under mild reaction conditions.

In our research on the synthesis of polycyclic aromatic hydrocarbons and their derivatives, we suggested new and facile synthetic methods for phenanthrene ring with regioselectivity. We envisioned that phenanthrene construction can be derived from ortho-propargyl biaryl derivative via transition metal-catalyzed intramolecular cyclization. The derivatives investigated showed a preference 6-endo cyclization over 5-exo mode, not observable in 7-endo-mode. The complex produces construction of the phenanthrene with a vinyl metal functional unit. The subsequent loss of hydroxyl group would afford α,β-unsaturated carbene functionality, thereby the competing the formation of the phenanthrene system. With the possibility of various transformation of the carbene, this intermediate underwent 1,2-H migration to afford vinylphenanthrene product. To demonstrate the pathway via a carbene intermediate in this reaction, the substrate which blocks of a 1,2-H migration was prepared. This substrate would respectively give the phenanthrene product, which reacted with acidic C–H bonds in good yield, resulting a platinum carbene intermediate is a key complex of the transformation for the synthesis of polycyclic aromatic hydrocarbons.

**Key words:** Phenanthrene, biphenyl propargyl alcohol, PtCl₂, platinum-carbene complex

**Student number:** 2013 – 21579
II. Introduction

Polycyclic aromatic hydrocarbons have received attention, especially in materials science, because of their utility in photoelectronic devices such as field-effect transistors, light emitting diodes, and solar cells. Most of the group consist of phenanthrene molecules within a large number of natural and non-natural compounds are common in biologically activity. A variety of approaches for the development of their backbone have been established. Among the different methods reported so far, the developments based on metal catalyst are of important value as they generally offer an selective and efficient routes to functionalized phenanthrene derivatives directly from simple substrates in fewer steps and under mild reaction conditions.

Among the variety of synthetic approaches to phenanthrenes, the transition metal-induced cyclization of easily prepared ortho-functionalized biaryl-type precursor has attracted attention because of its ability to expansion of poly-substituted phenanthrenes. Example of the synthesis based on metal mediated carbocyclization reaction of alkyndlated biaryl substrates are known in the literatures (Scheme 1). In the iron induced hydroarylation of alkyne reported by Takaki et al, a vinyl cation intermediate rendered phenanathrene framework (Scheme 1, eq 1). Takaki et al suggested that the progress reaction strongly depended on the electronic character of two aryls. In the metal-mediated reaction, metal ion generally coordinates to the triple bond and induces nucleophile attack of an aromatic ring. Although the carbocyclization reaction allowed for significant structural variation, it inherently possessed a regioselective competition depending on the metal catalysts and the substrate types. From the pioneering studies of Furstner et al, ortho-alkynyl biaryls were converted into substituted phenanthrenes with catalytic amounts of PtCl₂, AuCl₃, GaCl₃, and InCl₃ (Scheme 1, eq 2). In this reaction condition, the substrates investigated showed the competition between 5-exo or 6-endo mode following the reaction pathways. To overcome the selectivity, Kim et al reported that ortho-propargyl biaryls with InCl₃ in toluene were rapidly transformed to six-membered ring through cycloisomerization (Scheme 1, eq 3). The possibility of competing cyclization modes of 6-endo-dig and 7-endo-dig could be overcome by Baldwin’s rules.

During the course of our research on the synthesis of polycyclic aromatic hydrocarbons and their derivatives, we required new and facile synthetic methods for phenanthrene ring with regioselectivity. We envisioned that phenanthrene construction can be derived from ortho-propargyl biaryl derivative 1.
via transition metal-catalyzed intramolecular cyclization (Scheme 1, eq 4). The subsequent loss of hydroxyl group would afford \( \alpha,\beta \)-unsaturated carbene functionality, thereby the competing the formation of the phenanthrene system.

Scheme 1. Proposed strategy for synthesis of phenanthrene
III. Results and Discussion

The easily accessible biaryl propargyl alcohol 1a was initially prepared as the model substrate to probe the viability and outcome of the envisaged synthesis of phenanthrene skeleton. The preparation of the substrate was depicted in Scheme 2. To prepare the model substrate, 3,5-dimethoxyboronic acid 2 was subjected to a Suzuki-coupling reaction with 2-bromo benzaldehyde 3 to give the biphenyl derivative 4 in good yield. Prepared 4 formyl group was extended with the required alkyne group 5 to finally provide the standard substrate 1a. The lithiated alkyne 5 can also be diverted to the synthesis of other substrates for ortho-propargyl alcohol biaryls.

Scheme 2. Representative example for the preparation of the required substrate

In this model substrate, a simple cyclopentyl group was attached to the alkyne terminal to avoid complexity during the cyclization process. The ortho-propargyl biaryl derivative 1a was obtained via addition of alkynyl aldehyde to the prepared biaryl terminal alkyne. Various transition metal catalysts (10 mol%) were screened in toluene (0.05 M) at 80 °C (oil bath) to induce a desired cyclization adduct (Table 1).

The set of entries investigated showed a competition between 6-endo and 5-exo cyclization, not observable in 7-endo-mode. A Pd(OAc)_2 metal catalyst was failed to give the desired product, and recovery of the starting material or decomposition was observed (entry 1). When InCl_3 was employed, the reaction was processed in good conversion of starting material, but it only afforded the undesired product fluorene 5a (entry 2). The reactions using more carbophilic Au salt, such as AuCl and AuCl_3, gave the desired phenanthrene 4a in low yield. In addition, substantial amounts of fluorene 5a were also formed (entries 5 and 6).
Among the tested metal species, Pt salts most efficiently induced the desired 6-endo-cyclization. Under the screening conditions, the use of PtCl$_2$ resulted in the formation of phenanthrene 4a in 1h in excellent yield (98%) without noticeable formation of any side products (entry 3). Other Pt salt, such as PtCl$_4$, afforded the desired product with satisfactory results. However, this salt was found to be less effective than PtCl$_2$ with respect to reaction yield and selectivity (entry 4). Upon changing the solvent to DCE and THF with PtCl$_2$, the desired adduct was formed, but the yield and selectivity were slightly lower (entries 7 and 8). This results seemed to be seen that the catalyst having “soft” character could be blocked elimination of hydroxyl group before the cyclization.

With this optimal conditions in hand, we examined the substrate scope of this reaction. We first investigated analogues biaryl propargyl alcohols having various attached functional groups (Scheme 2). All of the examined substrates showed exclusive preference for the 6-endo cyclization over the conceivable 5-exo mode, following cyclization pathway. The reaction of alkyne 1b bearing a propyl group afforded the mono-substituted vinylphenanthrene 4b in excellent yield. The reaction of this

<table>
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<th>solvent</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>yield$^b$ (%)</th>
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$^a$Reaction condition : Starting material 1a (0.1 mmol) and metal catalyst (0.01 mmol, 10 mol%) in solvent (2mL). $^b$Yield determined by $^1$H NMR using 1,1,2,2-tetrachloroethane as the internal standard. The value in parentheses indicates the isolated yield.
<table>
<thead>
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<th>product</th>
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<td><img src="image" alt="1i" /></td>
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<td>12</td>
<td><img src="image" alt="4j" /></td>
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</tbody>
</table>

^aReaction condition: Starting material 1 (0.1 mmol) and PtCl₂ (0.01 mmol, 10 mol%) in toluene (2 mL)

^bUndesired fluorene was formed the 40%. The ration of 6-endo : 5-exo = 1:1
substrate afforded a mixture of \( Z \) and \( E \) isomers in a 3:1 ratio. Other primary alkyl group substituted alkynes 1c–f readily produced the corresponding products in high yield and with similar \( Z/E \) ratios.\(^9\) The successful results obtained with substrate 1c–f illustrated the good functional group tolerance and the potential usefulness of the reaction, as these substrates possessed synthetically valuable functional groups, such as a silyl-protected alcohol, \( N \)-phthalimide-protected amine, and ester group.\(^10\) The benzyl substrate 1g also successfully converted into phenanthrene 4g, but the \( Z/E \) ratio of the isomers was only 1:1. When an electron-donating methyl group was present on the benzene ring, the \( Z/E \) ratio of the product (4h and 4i) was not significantly changed in 4h. Prolonged reaction time served as a conformational change by regulating the \( Z/E \) ratio of the products (Scheme 4). When an eletron-withdrawing trifluoromethyl group substituted in the ortho position, however, the \( Z/E \) ratio of the product 4j changed 1:3. Although it is difficult to rationalize the subtle outcome of the individual results, the electronic effect would slightly influence the \( Z/E \) ratio of the products when the reaction was completed, not directly affected by steric effect. The reaction with the substrate 1j was not converted into a mixture of product 4j within 12 h, thus the reaction of platinum-mediate cyclization could not compared with the reaction of electron-donating substrates (4h and 4i).

**Scheme 4. The effect of the \( E/Z \) ratio determination**

<table>
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<th>( E/Z ) ratio</th>
<th>( E/Z ) ratio</th>
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<tr>
<td>4h</td>
<td>1h (o-Me)</td>
<td>1i (p-Me)</td>
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<td>4h</td>
<td>( E/Z = 1:1.4 )</td>
<td>( E/Z = 1:1.4 )</td>
</tr>
<tr>
<td>48h</td>
<td>1h (o-Me)</td>
<td>1i (p-Me)</td>
</tr>
<tr>
<td>4h</td>
<td>( E/Z = 1:4.5 )</td>
<td>( E/Z = 1:5 )</td>
</tr>
</tbody>
</table>

The further explore the reaction scope, the reaction was extended to different biaryl systems (Scheme 6). The substrate bearing electron-donating groups, such as 3,4-methylenedioxy or 3,4-dimeyhoxy groups, on the upper ring of the biphenyl backbone underwent smooth cyclization to afford phenanthrene products 4k and 4l in high yield. However, the reaction required longer time compared with that of the 3,5-dimethoxy substrate 1a. The reaction of 3-methoxy functionalized substrate afforded a 5:1 regiochemical mixture of phenanthrene products 4m and 4m', favoring cyclization on the less hindered position. To check the efficiency of this reaction, tertiary alcohol substrate 1n was prepared and evaluated (Scheme 5). The substrate 1n was prepared by addition of lithiated cyclopentyl
group to ortho-methyl ketone biaryl 6 which was inseparable in 50% yield. To isolate the product, the mixture was immediately reduced by NaBH₄, thus a reduced simple secondary alcohol 7 could be separated from the crude. A substrate synthesized with biaryl propargyl tertiary alcohol 1n was converted into phenanthrene product 4n, but having only 40% of conversion because of steric hinderance of leaving group. An undesired product fluorene product 8 was produced in 40%. While some of the electron-rich substrates were converted in reasonable yield, substrate 4o with unfunctionalized biaryl backbone and substrate 4p with 2-methoxy group failed to produce the desired phenanthrene products, even under prolonged high temperature conditions, due to lower nucleophilicity of its aryl ring. Substrate 1q was successfully converted into pyrene 4q to prove the generality of this novel method.

**Scheme 5. Preparation of substrate and the reaction of 1n**
Scheme 6. Substrate Scope of Biaryl Propargyl Alcohols (1k–q)\textsuperscript{a}

<table>
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<th>entry</th>
<th>starting material</th>
<th>time (h)</th>
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<th>yield (%)</th>
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</table>

\textsuperscript{a}Reaction codition: Starting material I (0.1 mmol) and PtCl\textsubscript{2} (0.01 mmol, 10 mol%) in toluene (2 mL)

\textsuperscript{b}Determined by \textsuperscript{1}H NMR analysis using 1,1,2,2-tetrachloroethane as the internal standard.

Scheme 7 illustrates the proposed mechanism for the production of substituted vinyl phenanthrenes 4. Addition of an electrophilic platinum to a biaryl derivative bearing alkyne unit at one of its ortho-positions engenders equilibrium between the substrate I and the metal complex I to induce nucleophilic attack by the aromatic ring. Metal-assisted intramolecular cyclization complex I
produces construction of the phenanthrene II with a vinyl metal functional unit. Subsequent loss of hydroxyl group with the assistance of the metal would give Pt-carbene intermediate III. This complex can transform other functionalities through various characteristic reactions of the carbene. However, the un-isolable intermediate III underwent 1,2-H migration to afford vinylphenanthrene product 4.

Scheme 7. Plausible Mechanistic Pathway for the Formation of Vinylphenanthrenes

To demonstrate the pathway via a carbene intermediate in this reaction, we prepared substrate 6a, in which a 1,2-H migration is not possible. With 10 mol% of PtCl$_2$ in toluene at 80 °C under N$_2$ atmosphere, the substrate 6a would respectively give the phenanthrene product 7a, which reacted with acidic C–H bonds in good yield (71%). These result suggested that a platinum carbene intermediate is a key complex of the transformation for the synthesis of polycyclic aromatic hydrocarbons (Scheme 8).
Scheme 8. C–H Insertion of Pt-Carbene Complex

\[
\text{BnO} \quad \text{O} \quad \text{Ph} \quad \text{Pt} \quad \text{Ph} \quad \text{BnO} \quad \text{O} \quad \text{Ph} \\
\text{BnO} \quad \text{O} \quad \text{Ph} \quad \text{Pt} \quad \text{Ph} \quad \text{BnO} \quad \text{O} \quad \text{Ph}
\]

\[\text{PtCl}_2 (10 \text{ mol } \%)
\text{toluene, } 80^\circ \text{C}
\text{18h, 71}\%
\]

\[\text{cat. Pt}
\text{C–H Insertion}
\]

\[
\text{BnO} \quad \text{O} \quad \text{Ph} \quad \text{Pt} \quad \text{Ph} \quad \text{BnO} \quad \text{O} \quad \text{Ph} \\
\text{BnO} \quad \text{O} \quad \text{Ph} \quad \text{Pt} \quad \text{Ph} \quad \text{BnO} \quad \text{O} \quad \text{Ph}
\]
IV. Conclusion

In conclusion, Pt-assisted intramolecular cyclization of biaryl propargyl alcohol substrates was investigated as highly regioselective new method for synthesis of phenanthrenes. Notable features of this method are readily available starting material, mild conditions and broad substrate scope. Most of the substrate showed selectivity for 6-endo cyclization by overcoming the conceivable of 5-, 6-, and 7-membered ring adducts. Mechanistic study revealed that this reaction presumably proceeds via platinum carbenoid. In the presence of a catalytic amount of PtCl₂, intramolecular cyclization and subsequent loss of hydroxyl group affords a phenanthrene skeleton with a carbene functional unit. The resulting carbene rapidly undergoes 1,2-H migration to give a vinylphenanthrene system. The reaction is accomplished under mild condition and concluded various important functional groups, thus allowing the synthesis of functionalized phenanthrenes. Moreover, the carbene intermediate can be confirmed by a migration blocked substrate, giving the C–H insertion of carbene.
V. Experimental

1. General

All chemicals were reagent grade and used as purchased. All reactions were performed under an inert atmosphere of dry nitrogen using distilled dry solvents. The reactions were monitored with TLC analysis using silica gel 60 F-254 thin layer plates. Compounds on the TLC plates were visualized under UV light and by spraying with either potassium permanganate or anisaldehyde solutions. Flash column chromatography was conducted on silica gel 60 (230–400 mesh). Melting points were measured using a Buchi B-540 melting point apparatus without correction. $^1$H NMR (300, 400, or 500MHz) spectra and $^{13}$C NMR (75, 100, or 125 MHz) spectra were recorded in δ units relative to the deuterated solvent. The IR spectra were measured on a Fourier Transform Infrared spectrometer. High-resolution mass spectra (HRMS) were recorded using FAB.

2. Preparation of the starting materials

Scheme S-1. General procedure for the preparation of biaryl aldehydes by Suzuki coupling$^{11}$

To a solution of bromobenzaldehyde (5.50 mmol, 1 equiv), phenylboronic acid (11.0 mmol, 2 equiv), and Pd(PPh$_3$)$_4$ (0.15 mmol, 0.03 equiv) in DME (28 mL) and EtOH (7 mL) was added a solution of Na$_2$CO$_3$ (12.1 mmol, 2 equiv) in water (7 mL) under nitrogen. The result mixture was refluxed
overnight and diluted with EtOAc. The organic layer was washed with saturated NH₄Cl solution and brine, dried over MgSO₄ and concentrated. The crude product was purified using column chromatography on silica gel (hexane/EtOAc), resulting in the desired product.

2-(3,5-Dimethoxyphenyl)benzaldehyde. Following the general procedure, the title compound was obtained as a white solid (11.6 g, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 9.99 (s, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.3Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 4.51 (s, 1H), 6.49 (s, 2H), 3.79 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 192.1, 160.5 (2C), 145.7, 139.6, 133.6, 133.3, 130.3, 127.7, 127.2, 108.3 (2C), 99.9, 55.3 (2C). These NMR data matched with the reported data.

2-(3,4-Methylenedioxyphenyl)benzaldehyde. Following the general procedure, the title compound was obtained as light yellow solid (1.28 g, 94% yield). ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.85 (s, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.02 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 192.4, 147.8, 147.7, 145.5, 133.8, 133.5, 131.5, 130.6, 127.6, 127.5, 124.1, 110.2, 108.2, 101.4; IR (neat, cm⁻¹) max 3066, 2893, 2753, 1692, 1473, 1246, 1223, 1039, 765; HRMS (FAB): calcd. for C₁₉H₁₈O₄ [M⁺] 310.1205, found 310.1204.

2-(3-Methoxyphenyl)benzaldehyde. Following the general procedure, the title compound was obtained as a colorless oil (1.27 g, 91% yield). ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 8.00 (d, J = 7.6 MHz, 1H), 7.60 (t, J = 7.3 MHz, 1H), 7.47 (t, J = 7.7 MHz, 1H), 7.43 (d, J = 7.7 MHz, 1H), 7.35 (t, J = 7.8 MHz, 1H), 6.96 (d, J = 8.3 MHz, 1H), 6.93 (d, J = 7.8 MHz, 1H), 6.90 (s, 1H), 3.82 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 192.3, 159.4, 145.7, 139.0, 133.6, 133.4, 130.5, 129.3, 127.7, 127.3, 122.6, 115.6, 113.5, 55.2. These NMR data
matched with the reported data.

2-(3,4-Dimethoxyphenyl)-4-methoxybenzaldehyde. Following the general procedure, the title compound was obtained as a white solid (7.8 g, 96% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.85 (s, 1H), 7.99 (d, $J$ = 8.8 MHz, 1H), 6.98–6.91 (m, 3H), 6.89–6.86 (m, 2H), 3.93 (s, 3H), 3.891 (s, 3H), 3.889 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.2, 163.4, 149.1, 148.7, 148.3, 130.3, 129.9, 127.4, 122.5, 115.2, 113.6, 112.9, 110.8, 56.0 (2C), 55.6. These NMR data matched with the reported data.

3',5'-Dimethoxy-[1,1'-biphenyl]-2,6-dicarbaldehyde. Following the general procedure, the title compound was obtained from 2-bromoisophthalaldehyde and 3,5-dimethoxyphenylboronic acid as a white solid (3.45 g, 80% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.83 (s, 2H), 8.21 (d, $J$ = 7.7 Hz, 2H), 7.63 (t, $J$ = 7.7 Hz, 1H), 6.56 (t, $J$ = 2.3 Hz, 1H), 6.5 (d, $J$ = 2.2 Hz, 2H), 3.80 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.8 (2C), 160.7 (2C), 148.0, 134.6, 134.3, 132.1 (2C), 128.3, 109.3 (2C), 100.6, 55.4 (2C).

2-(3,5-Dibenzyloxyphenyl)benzaldehyde. Following the general procedure, the title compound was obtained from 3,5-dibenzyloxy-bromobenzene and 2-formylphenylboronic acid as a white solid (989 mg, 93% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.98 (s, 1H), 8.01 (d, $J$ = 7.8 Hz, 1H), 7.61 (t, $J$ = 7.5 Hz, 1H), 7.48 (t, $J$ = 7.5 Hz, 1H), 7.44–7.37 (m, 9H), 7.34 (q, $J$ = 7.4 Hz, 2H), 6.70 (s, 1H), 6.61 (d, $J$ = 1.9Hz, 2H), 5.06 (s, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 192.2, 159.7 (2C), 145.7, 139.7, 136.4, 133.7, 133.4 (2C), 130.4, 128.6 (4C), 128.1 (2C), 127.8, 127.5 (4C), 127.3, 109.6 (2C), 101.7, 70.2 (2C); IR (neat, cm$^{-1}$) $\nu_{max}$ 3066, 3035, 2868, 2753, 1692, 1592, 1212, 1156, 1055, 698; HRMS (FAB): calcd. for C$_{19}$H$_{18}$O$_4$ [M]$^+$ 310.1205, found 310.1204.
Scheme S-2. General Procedure for the preparation of propargyl alcohol biaryls (1a–q, 6a) by addition of lithium acetylide.

To a solution of terminal alkyne (6.0 mmol, 2 equiv) in dry THF (25 mL) was added $n$-BuLi (3.75 mL, 6.0 mmol, 2 equiv, 1.6 M solution in hexane) at −78 °C under nitrogen. After the reaction mixture was stirred for 1 h at −78 °C, biaryl aldehyde (3.0 mmol, 1 equiv) in dry THF (5 mL) was added. The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with saturated NH$_4$Cl solution and extracted with EtOAc. The organic layers were washed with brine twice, dried over MgSO$_4$, filtered and concentrated. The crude product was purified using column chromatography on silica gel (hexane/EtOAc), resulting in the desired product.

3-Cyclopentyl-1-(3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ol (1a). Following the general procedure, compound 1a was obtained as a white solid (721 mg, 87% yield). m.p. 80–84 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, $J$ = 7.6 Hz, 1H), 7.41 (t, $J$ = 7.6 Hz, 1H), 7.33 (t, $J$ = 7.3 Hz, 1H), 7.26 (d, $J$ = 7.6 Hz, 1H), 6.58 (d, $J$ = 1.5 Hz, 2H), 6.46 (s, 1H), 5.48 (d, $J$ = 4.0 Hz, 1H), 3.79 (s, 6H), 2.65–2.59 (m, 1H), 2.07 (d, $J$ = 5.0 Hz, 1H), 1.92–1.84 (m, 2H), 1.69–1.61 (m, 2H), 1.61–1.51 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 160.4 (2C), 142.2, 140.7, 138.9, 129.7, 128.0, 128.0, 127.3, 107.6 (2C), 99.7, 91.5, 80.3, 61.9, 55.4 (2C), 33.7 (2C), 30.2, 25.0 (2C); IR (neat, cm$^{-1}$) $\nu$$_{max}$ 3469, 3060, 2959, 2872, 2840, 2236, 1595, 1458, 1205, 1155, 794; HRMS (FAB): calcd. for C$_{22}$H$_{34}$O$_3$ [M]$^+$ 336.1825, found 336.1720.
1-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)hex-2-yn-1-ol (1b). Following the general procedure, compound 1b was obtained as a colorless oil (3.9 g, 95% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.84 (d, J = 7.6 \text{ Hz}, 1\text{H}), 7.26 (d, J = 6.8 \text{ Hz}, 1\text{H}), 6.57 (d, J = 1.9 \text{ Hz}, 2\text{H}), 6.46 (s, 1\text{H}), 5.49–5.48 (m, 1\text{H}), 3.79 (s, 6\text{H}), 2.19 (td, J = 7.0 \text{ Hz}, 1.6 \text{ Hz}, 2\text{H}), 2.03 (d, J = 5.1 \text{ Hz}, 1\text{H}), 1.51 (qd, J = 14.5 \text{ Hz}, 7.2 \text{ Hz}), 0.95 (t, J = 7.4 \text{ Hz}, 3\text{H}); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 160.4 (2\text{C}), 142.2, 140.7, 138.9, 129.7, 128.1 (2\text{C}), 127.4, 127.3, 107.6 (2\text{C}), 99.7, 87.2, 81.0, 61.9, 55.4 (2\text{C}), 22.0, 20.9, 13.6; IR (neat, \(\mathrm{cm}^{-1}\)) \(\nu_{\text{max}} 3473, 3003, 2965, 2937, 2875, 2841, 2817, 1594, 1459, 1205, 1155, 1064, 846, 764; HRMS (FAB): calcd. for C\(_{19}\)H\(_{18}\)O\(_4\) [M]+ 310.1 205, found 310.1204.

7-((tert-Butyldimethylsilyl)oxy)-1-(3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)hept-2-yn-1-ol (1c). Following the general procedure, compound 1c was obtained as a colorless oil (1.0 g, 98% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.83 (d, J = 7.7 \text{ Hz}, 1\text{H}), 7.40 (t, J = 7.5 \text{ Hz}, 1\text{H}), 7.33 (t, J = 7.4 \text{ Hz}, 1\text{H}), 7.25 (d, J = 10.8 \text{ Hz}, 1\text{H}), 6.57 (d, J = 1.3 \text{ Hz}, 2\text{H}), 6.46 (s, 1\text{H}), 5.47 (s, 1\text{H}), 3.79 (s, 6\text{H}), 3.59 (t, J = 5.4 \text{ Hz}, 2\text{H}), 2.25 (t, J = 6.4 \text{ Hz}, 2\text{H}), 2.03 (d, J = 4.6 \text{ Hz}, 1\text{H}), 1.57–1.52 (m, 4\text{H}), 0.86 (s, 9\text{H}), 0.01 (s, 6\text{H}); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 160.5 (2\text{C}), 142.2, 140.7, 138.9, 129.7, 128.1 (2\text{C}), 127.4, 127.3, 107.7 (2\text{C}), 99.7, 87.2, 81.0, 62.6, 61.9, 55.4 (2\text{C}), 32.0, 25.9 (3\text{C}), 25.1, 18.7, 18.3, –5.3 (2\text{C}); IR (neat, \(\mathrm{cm}^{-1}\)) \(\nu_{\text{max}} 3453, 3002, 2953, 2860, 1594, 1464, 1253, 1155, 1104, 835, 763; HRMS (FAB): calcd. for C\(_{27}\)H\(_{38}\)O\(_4\)Si [M]+ 454.2539, found 454.2533.

1-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)-4-phenylbut-2-yn-1-ol (1g). Following the general procedure, compound 1g was obtained as a yellow oil (180 mg, 76% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.87 (d, J = 7.6 \text{ Hz}, 1\text{H})\), 7.42 (t, J = 7.3 \text{ Hz}, 1\text{H}), 7.35 (t, J = 7.2 \text{ Hz}, 1\text{H}), 7.29–7.26 (m, 5\text{H}), 7.24–7.20 (m, 1\text{H}), 6.57 (d,
$J = 2.1 \text{ Hz}, 2\text{H}$, 6.46 (s, 1H), 5.55 (s, 1H), 3.76 (s, 6H), 3.64 (s, 2H), 2.11 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.5 (2C), 142.2, 140.7, 138.7, 136.4, 129.8, 128.5 (2C), 128.2, 128.1, 127.9 (2C), 127.3, 126.6, 107.6 (2C), 99.7, 84.7, 83.0, 61.9, 55.4 (2C), 25.2; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3452, 3064, 3030, 3005, 2940, 2840, 1594, 1204, 1154, 843, 764; HRMS (FAB): calcd. for C$_{24}$H$_{22}$O$_3$ [M]$^+$ 358.1569, found 359.1581.

1-(2-(Benzo[d][1,3]dioxol-5-yl)phenyl)-3-cyclopentylprop-2-yn-1-ol (1k).

Following the general procedure, compound 1k was obtained as a colorless oil (268 mg, 95% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J = 7.6$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.3$ Hz, 1H), 7.21 (d, $J = 7.5$ Hz, 1H), 6.92 (s, 1H), 6.85 (d, $J = 1.8$ Hz, 1H), 6.85 (t, $J = 9.4$ Hz, 1H), 5.98 (s, 2H), 5.45 (s, 1H), 2.65–2.62 (m, 1H), 2.04 (s, 1H), 1.92–1.87 (m, 2H), 1.69–1.62 (m, 2H), 1.62–1.52 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.4, 146.9, 140.5, 139.1, 134.1, 130.2, 128.0, 127.8, 127.3, 122.9, 110.2, 108.0, 101.1, 91.6, 80.2, 61.9, 33.7 (2C), 30.2, 25.0 (2C); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3423, 3063, 2958, 2872, 2779, 2229, 1607, 1476, 1220, 1037, 758; HRMS (FAB): calcd. for C$_{21}$H$_{20}$O$_3$ [M]$^+$ 320.1412, found 320.1419.

3-Cyclopentyl-1-(3',4',5-trimethoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ol (1l). Following the general procedure, compound 1l was obtained as a yellow oil (237 mg, 88% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, $J = 8.6$ Hz, 1H), 7.01 (s, 1H), 6.98–6.89 (m, 3H), 6.79 (d, $J = 2.4$ Hz, 1H), 5.38 (d, $J = 4.1$ Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 2.65–2.61 (m, 1H), 2.02 (d, $J = 5.2$ Hz, 1H), 1.92–1.87 (m, 2H), 1.68–1.62 (m, 2H), 1.60–1.51 (m, 4H); $^{13}$C NMR (100 Hz, CDCl$_3$) δ 159.1, 148.43, 148.42, 142.1, 132.9, 131.7, 128.9, 121.5, 115.1, 113.4, 112.9, 110.9, 91.2, 80.5, 61.6, 55.94, 55.89, 55.4, 33.7 (2C), 30.2, 25.0 (2C); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3495, 2958, 2872, 2838, 1606, 1517, 1493, 1252, 1141, 1028, 816, 764; HRMS (FAB): calcd. for C$_{23}$H$_{26}$O$_4$ [M]$^+$ 366.1831, found 366.1825.
3-Cyclopentyl-1-(3'-methoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ol (1m).

Following the general procedure, compound 1m was obtained as a light yellow oil (168 mg, 91% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, $J = 7.8$ Hz, 1H), 7.41 (t, $J = 7.4$ Hz, 1H), 7.34 (t, $J = 7.1$ Hz, 1H), 7.31 (t, $J = 7.8$ Hz, 1H), 7.26 (d, $J = 8.3$ Hz, 1H), 6.99 (d, $J = 7.1$ Hz, 1H), 6.98 (s, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 5.46 (d, $J = 4.1$ Hz, 1H), 3.82 (s, 3H), 2.65–2.60 (m, 1H), 2.05 (d, $J = 5.2$ Hz, 1H), 1.92–1.84 (m, 2H), 1.69–1.61 (m, 2H), 1.59–1.51 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.2, 141.6, 140.6, 138.9, 129.9, 129.1, 128.03, 127.98, 127.3, 121.9, 114.9, 113.1, 91.5, 80.2, 61.9, 55.2, 33.7 (2C), 30.2, 25.0 (2C); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3433, 3062, 2958, 2871, 2228, 1598, 1476, 1214, 755; HRMS (FAB): calcd. for C$_{21}$H$_{22}$O$_2$ [M]+ 306.1620, found 306.1625.

1-([1,1'-Biphenyl]-2-yl)-3-cyclopentylprop-2-yn-1-ol (1o). Following the general procedure, compound 1o was obtained as a colorless oil (808 mg, 96% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, $J = 7.6$ Hz, 1H), 7.42 (s, 4H), 7.36 (dd, $J = 14.0$ Hz, 7.4 Hz, 2H), 7.25 (d, $J = 7.9$ Hz, 1H), 5.43 (d, $J = 2.6$ Hz, 1H), 2.66–2.60 (m, 1H), 2.05 (d, $J = 4.9$ Hz, 1H), 1.92–1.85 (m, 2H), 1.75–1.68 (m, 2H), 1.62–1.52 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.8, 140.3, 139.0, 130.1, 129.5 (2C), 128.1 (2C), 128.0, 127.9, 127.29, 127.25, 91.5 , 80.2, 61.9, 33.7 (2C), 30.2, 25.0 (2C); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3419, 3062, 3028, 2962, 2248, 2231, 1478, 1263, 926; HRMS (FAB): calcd. for C$_{17}$H$_{14}$O$_2$ [M]+ 250.0994, found 250.0998.

3-Cyclopentyl-1-(2'-methoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ol (1p).

Following the general procedure, compound 1p was obtained as a colorless oil (347 mg, 95% yield). Two conformers are existed (2:1 mixture) due to hydrogen bonding between methoxy group in phenyl and hydroxyl group in alkynyl bond. $^1$H NMR
(400 MHz, CDCl$_3$) δ 7.89 (d, $J = 5.8$ Hz, 2H), 7.79 (d, $J = 5.6$ Hz, 1H), 7.46–7.34 (m, 3H), 7.24–7.23 (m, 1H), 7.19–7.12 (m, 3H), 7.04 (t, $J = 5.3$ Hz, 2H), 6.98 (q, $J = 6.8$ Hz, 4H), 5.29–5.26 (m, 3H), 3.75 (s, 6H), 3.73 (s, 6H), 3.02 (d, $J = 1.5$ Hz, 2H), 2.65–2.59 (m, 3H), 2.15 (d, $J = 4.3$ Hz, 2H) 1.93–1.81 (m, 6H), 1.72–1.63 (m, 6H), 1.63–1.45 (m, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 156.1, 156.0, 140.3, 139.9, 137.0, 136.8, 131.6, 131.5, 130.6, 130.2, 129.5, 129.2, 129.1, 128.3, 128.15, 128.11, 128.0, 127.5, 127.4, 121.3, 120.6, 111.2, 110.7, 91.0, 90.5, 62.8, 55.8, 55.4, 33.71, 33.65, 30.20, 30.17, 25.0 (2C).

1,1'-[(3',5'-Dimethoxy-[1,1'-biphenyl]-2,6-diyl)bis(3-cyclopentyl)prop-2-yn-1-ol] (1q). Following the general procedure, compound diastereomeric mixture 1q was obtained as a colorless oil and a white solid (320 mg, 95% yield). Diastereomer 1: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.78 (d, $J = 7.7$ Hz, 2H), 7.47 (t, $J = 7.8$ Hz, 1H), 5.20 (dd, $J = 4.8$ Hz, 1.8 Hz, 2H), 2.63–2.55 (m, 2H), 1.95 (d, $J = 4.9$ Hz, 1H), 1.88–1.83 (m, 4H), 1.72–1.49 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.5 (2C), 139.8 (2C), 138.8, 138.6, 128.6, 126.8 (2C), 108.2 (2C), 100.0, 91.4, 80.0, 62.0 (2C), 55.4 (2C), 33.7 (4C), 30.2 (2C), 25.0 (4C). Diastereomer 2: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.79 (d, $J = 7.8$ Hz, 2H), 7.47 (t, $J = 7.8$ Hz, 1H), 6.49–6.41 (m, 3H), 5.19 (dd, $J = 5.1$ Hz, 1.8 Hz, 2H), 3.78 (d, $J = 6.2$ Hz, 1H), 2.63–2.58 (m, 2H), 1.92 (d, $J = 7.8$ Hz, 2H), 1.88–1.86 (m, 4H), 1.68–1.50 (m, 8H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 160.5, 160.3, 139.7 (2C), 138.72, 138.67, 128.6, 126.9 (2C), 108.4, 108.0, 99.9, 91.3, 79.9, 62.0 (2C), 55.4, 55.3, 33.7 (4C), 60.2 (2C), 25.0 (4C).
1-(3',5'-Bis(benzyloxy)-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-ol (6a).

Following the general procedure, compound 1x was obtained as a light yellow oil (544 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, $J = 7.6$ Hz, 1H), 7.47–7.36 (m, 12H), 7.34–7.25 (m, 6H), 6.75 (d, $J = 1.8$ Hz, 2H), 6.69 (s, 1H), 5.69 (d, $J = 4.0$ Hz, 1H), 5.07 (s, 4H), 2.20 (d, $J = 4.4$ Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.6 (2C), 142.1, 140.6, 138.2, 136.7 (2C), 131.6 (2C), 129.8, 128.5 (4C), 128.4, 128.24, 128.21 (3C), 128.1, 127.9 (2C), 127.4 (4C), 122.5, 108.7 (2C), 101.5, 89.7, 86.3, 70.0 (2C), 62.2; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3437, 3064, 3033, 2872, 1591, 1491, 1210, 1150, 1052, 1015, 755, 693; HRMS (FAB): calcd. for C$_{35}$H$_{28}$O$_3$ [M]$^+$ 496.2038, found 496.2033.

Scheme S-3. Preparation of propargyl alcohol biaryl derivative 1d.

7-Chloro-1-(3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)hept-2-yn-1-ol. To a solution of 6-chloro-1-hexyne (600 µL, 4.95 mmol) in dry THF (20 mL) was added n-BuLi (3.1 mL, 4.96 mmol, 1.6 M solution in hexane) at –78 °C under nitrogen. After the reaction mixture was stirred for 1 h at –78 °C, 2-(3,5-dimethoxyphenyl)benzaldehyde (600 mg, 2.48 mmol) in dry THF (5 mL) was added. The reaction mixture was warmed to room temperature and stirred for 1h. The reaction was quenched with saturated NH$_4$Cl solution and extracted with EtOAc. The organic layers were washed with brine twice,
dried over MgSO$_4$, filtered and concentrated. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 3:1), resulting in the desired product as a colorless oil (842 mg, 95% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J$ = 7.7 Hz, 1H), 7.41 (t, $J$ = 7.4 Hz, 1H), 7.34 (t, $J$ = 7.4 Hz, 1H), 7.26 (d, $J$ = 7.5 Hz, 1H), 6.56 (d, $J$ = 1.8 Hz, 1H), 6.47 (s, 1H), 5.48 (s, 1H), 3.80 (s, 6H), 3.53 (t, $J$ = 6.5 Hz, 2H), 2.27 (t, $J$ = 6.4 Hz, 2H), 2.07 (brs, 1H), 1.86 (pentet, $J$ = 7.0 Hz, 2H), 1.65 (pentet, $J$ = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.5 (2C), 142.2, 140.7, 138.8, 129.8, 128.1, 128.1, 127.3, 107.7 (2C), 99.6, 86.3, 81.5, 61.8, 55.4 (2C), 44.5, 31.5, 25.7, 18.2; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3464, 3063, 3003, 2942, 2869, 2841, 1593, 1204, 1154, 1063, 842, 764; HRMS (FAB): calcd. for C$_{21}$H$_{23}$ClO$_3$ [M]$^+$ 358.1336, found 358.1340.

2-(7-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)-7-hydroxyhept-5-yn-1-yl)isoindoline-1,3-dione (1d). To a solution of 7-chloro-1-(3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)hept-2-yn-1-ol (100 mg, 0.278 mmol) in dry DMF (6 mL) was added phthalimide potassium salt (62 mg, 0.334 mmol) and KI (4.6 mg, 0.028 mmol). After the reaction mixture was stirred for 2 h at 100 °C, the reaction was quenched with H$_2$O and extracted with EtOAc. The organic layers were washed with brine twice, dried over MgSO$_4$, filtered and concentrated. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 1:1), resulting in the desired product 1d as a colorless oil (105 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82–7.80 (m, 3H), 7.71–7.68 (m, 2H), 7.39 (t, $J$ = 7.5 Hz, 1H), 7.32 (t, $J$ = 7.4 Hz, 1H), 7.25 (d, $J$ = 5.7 Hz, 1H), 6.56 (d, $J$ = 2.2 Hz, 2H), 6.45 (s, 1H), 5.46 (s, 1H), 3.79 (s, 6H), 3.69 (t, $J$ = 7.1 Hz, 2H), 2.37 (s, 1H), 2.28 (t, $J$ = 6.9 Hz, 2H), 1.79 (pentet, $J$ = 7.4 Hz, 2H), 1.54 (pentet, $J$ = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.4 (2C), 160.4 (2C), 142.2, 140.7, 138.8, 133.9 (2C), 132.1, 129.7 (2C), 128.1, 128.0, 127.4, 123.2 (2C), 107.6 (2C), 99.7, 86.2, 81.7, 61.8, 55.4 (2C), 37.4, 27.5, 25.4, 18.3; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3468, 3005, 2943, 2841, 1771, 1708, 1594, 1421, 1398, 1205, 1155, 1063, 1029, 846, 764, 720; HRMS (FAB): calcd. for C$_{30}$H$_{27}$NO$_5$ [M]$^+$ 469.1889, found 469.1883.

![Diagram of the compound](image-url)
Scheme S-4. Preparation of propargyl alcohol biaryl derivative 1e and 1f.

7-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)-7-hydroxyhept-5-ynoic acid (1e). To a stirred solution of triisopropylsilyl 7-(3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)-7-hydroxyhept-5-ynoate (290 mg, 0.568 mmol) in THF (2 mL) and MeOH (1 mL) was added K$_2$CO$_3$ (157 mg, 1.70 mmol) in H$_2$O (1 mL) under nitrogen. The mixture was stirred for 5 h at room temperature and acidified with 1N HCl. The organic layer was washed with Brine and extracted with EtOAc. The crude mixture was purified using column chromatography (CH$_2$Cl$_2$/MeOH, 10:1) resulting in the desired product 1e as a light yellow oil (168 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J$ = 7.6 Hz, 1H), 7.40 (t, $J$ = 7.5 Hz, 1H), 7.33 (t, $J$ = 7.4 Hz, 1H), 7.25 (d, $J$ = 8.9 Hz, 1H), 6.56 (d, $J$ = 1.9 Hz, 2H), 6.46 (s, 1H), 5.47 (s, 1H), 3.79 (s, 6H), 2.44 (t, $J$ = 7.3 Hz, 2H), 2.30 (t, $J$ = 6.7 Hz, 2H), 1.81 (pentet, $J$ = 7.1 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 178.7, 160.4 (2C), 142.1, 140.6, 138.6, 129.7, 128.1 (2C), 127.3, 107.7 (2C), 99.6, 85.7, 81.9, 61.8, 55.4 (2C), 32.7, 23.4, 18.2; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3025, 2953, 2236, 1948, 1712, 1434, 1249, 1069, 746, 701; HRMS (FAB): calcd. for C$_{21}$H$_{22}$O$_5$ [M]$^+$ 354.1467, found 354.1472.

7-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)-7-hydroxyhept-5-ynoate (1f). To a stirred solution of acid 1e (100 mg, 0.28 mmol) in toluene (1.8 mL) and MeOH (1.2 mL) was added TMSCHN$_2$ (180 $\mu$L, 0.37
mmol, 2.0 M solution in Et₂O) under nitrogen. The mixture was stirred at room temperature and quenched with water. The organic layer washed with Brine and extracted with EtOAc. The crude mixture was purified using column chromatography (hexane/EtOAc, 5:1) resulting in the desired product 1f as a colorless oil (90.4 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, 2H, J = 7.6 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.25 (d, J = 9.8 Hz, 1H), 6.56 (d, J = 1.6 Hz, 2H), 6.46 (s, 1H), 5.47 (s, 1H), 3.79 (s, 6H), 3.63 (s, 3H), 2.39 (t, J = 7.4 Hz, 2H), 2.30–2.27 (m, 1H), 2.28 (t, J = 7.0 Hz, 2H), 1.80 (pentet, J = 7.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 160.4 (2C), 142.1, 140.6, 138.7, 129.7, 128.1 (2C), 127.3, 107.6 (2C), 99.6, 85.7, 81.8, 61.7, 55.3 (2C), 51.5, 32.8, 23.6, 18.3; IR (neat, cm⁻¹) νmax 3457, 3002, 2953, 2913, 2841, 1736, 1594, 1337, 1205, 1063, 1026, 765; HRMS (FAB): calcd. for C₂₂H₂₄O₅ [M]⁺ 368.1624, found 368.1621.

**Scheme S-5. Preparation of propargyl alcohol biaryl derivative 1h and 1i**

1-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ol. To a solution of 2-(3,5-dimethoxyphenyl)benzaldehyde (3.0 g, 12.4 mmol) in dry THF (31 mL) was added 1-ethynylmagnesium bromide (49.5 mL, 24.8 mmol, 0.5 M solution in THF) at –78 °C under nitrogen. After the reaction mixture was stirred for 2 h at –78 °C, the reaction was quenched with saturated NH₄Cl solution and extracted with EtOAc. The organic layers were washed with brine twice, dried over MgSO₄, filtered and concentrated. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 4:1), resulting in the desired product as a white solid (3.1 g, 94% yield). m.p. 131–132 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, 1H, J = 7.6 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.28 (d, J = 7.4 Hz, 1H), 6.56 (s, 2H), 6.48 (s, 1H),
5.50 (d, $J = 3.3$ Hz, 1H), 3.79 (s, 6H), 2.60 (s, 1H), 2.34 (d, $J = 5.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.3 (2C), 141.9, 140.6, 137.8, 129.6, 128.2, 128.0, 127.2, 107.5 (2C), 99.6, 84.5, 74.4, 61.2, 55.2 (2C); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3430, 3286, 3004, 2941, 2841, 1592, 1420, 1204, 1152, 842, 764; HRMS (FAB): calcd. for C$_{17}$H$_{16}$O$_3$ [M]$^+$ 268.1099, found 268.1092.

1-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)-4-(o-tolyl)but-2-yn-1-ol (1h).

To a solution of 1-(3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ol (213 mg, 0.796 mmol), 2-methylbenzyl bromide (160 µL, 1.19 mmol) in MeCN (4 mL) was added CuI (152 mg, 0.796 mmol), TBAI (294 mg, 0.796 mmol) and K$_2$CO$_3$ (220 mg, 1.59 mmol) under nitrogen. The result mixture was heated for 1.5h at 60 °C and diluted with EtOAc. The organic layer was washed with saturated NH$_4$Cl solution and brine, dried over MgSO$_4$ and concentrated. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 15:1), resulting in the desired product 1x as a yellow oil (210 mg, 71% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.4$ Hz, 1H), 7.38–7.34 (m, 2H), 7.29 (d, $J = 7.4$ Hz, 1H), 7.18–7.14 (m, 3H), 6.59 (d, $J = 1.5$ Hz, 2H), 6.48 (s, 1H), 5.56 (s, 1H), 3.76 (s, 6H), 3.57 (s, 2H), 2.29 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 160.4 (2C), 142.1, 140.6, 138.7, 135.8, 134.6, 130.0, 129.7, 128.2, 128.0, 127.3, 126.8, 126.1 (2C), 107.5 (2C), 99.7, 84.2, 83.1, 61.8, 55.3 (2C), 23.3, 19.2; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3456, 3066, 3005, 2940, 2840, 2251, 1730, 1592, 1204, 1153, 907, 728; HRMS (FAB): calcd. for C$_{25}$H$_{24}$O$_3$ [M]$^+$ 371.1725, found 372.1710.

1-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)-4-(p-tolyl)but-2-yn-1-ol (1i). To a solution of 1-(3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ol (215 mg, 0.802 mmol), 4-methylbenzyl bromide (223 mg, 1.20 mmol) in MeCN (4 mL) was added CuI (153 mg, 0.802 mmol), TBAI (296 mg, 0.802 mmol) and K$_2$CO$_3$ (222 mg, 1.60 mmol) under nitrogen. The result mixture was heated for 1.5h at 60 °C and...
diluted with EtOAc. The organic layer was washed with saturated NH₄Cl solution and brine, dried over MgSO₄ and concentrated. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 15:1), resulting in the desired product 1x as a yellow oil (197 mg, 64% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H), 7.14 (dd, J = 34.8 Hz, 7.7 Hz, 4H), 6.59 (s, 2H), 6.49 (s, 1H), 5.56 (s, 1H), 3.76 (s, 6H), 3.60 (s, 2H), 2.31 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 160.3, 142.1, 140.6, 138.7, 136.1, 133.2, 129.7, 129.1 (2C), 128.0 (2C), 127.7 (2C), 127.3, 107.5 (2C), 99.7, 84.9, 82.8, 61.8, 55.3 (2C), 24.8, 21.0; IR (neat, cm⁻¹) νmax 3450, 3054, 3005, 2940, 2840, 2250, 1730, 1592, 1420, 1204, 1153, 907, 728; HRMS (FAB): calcd. for C₂₅H₂₄O₃ [M]⁺ 371.1725, found 372.1715.

**Scheme S-6.** Preparation of propargyl alcohol biaryl derivative 1j

![Scheme S-6](image)

1-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)-4-(2-(trifluoromethyl)phenyl)but-2-en-1-ol (1j). To a solution of 1-(3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)prop-2-en-1-ol (200 mg, 0.745 mmol), PdCl₂(CH₃CN)₂ (3.9 mg, 0.015 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (21 mg, 0.045 mmol), and Cs₂CO₃ (267 mg, 0.820 mmol) in THF (2 mL) was added 2-trifluoromethylbenzyl chloride (163 μL, 1.12 mmol) under nitrogen. The resulting mixture was heated for 2.5 h at 55 °C and diluted with EtOAc. The organic layer was washed with a saturated NH₄Cl solution and brine, dried over MgSO₄ and concentrated. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 4:1), to afford the desired product 1j as a yellow oil (212 mg, 67%). ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.43 (td, J = 7.5 Hz, 1.0 Hz, 1H), 7.36 (td, J = 7.6 Hz, 1.1 Hz, 1H), 7.33 (t, J
Scheme S-7. Preparation of biaryl propargyl tertiary alcohol derivative 1n

To a stirred solution of cyclopentylacetylene (1.30 mL, 2.11 mmol) in dry THF was added n-BuLi (270 µL, 2.34 mmol, 1.6 M solution in THF) at –78 °C under nitrogen. After the reaction mixture was stirred for 1 h at –78 °C, 1-(3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)but-3-yn-2-ol (200 mg, 0.780 mmol) was added and stirred for 15 h at room temperature. The reaction was quenched with saturated NH₄Cl solution and extracted with EtOAc. The organic layers were washed with brine twice, dried over MgSO₄, filtered and concentrated. To separate the product, the mixture was reduced with NaBH₄ (23.6 mg, 0.624 mmol). The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 3:1), resulting in the desired product as a colorless oil (137 mg, 50% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 5.9 Hz, 1H), 7.33 (t, J = 5.7 Hz, 1H), 7.26 (t, J = 5.6 Hz, 1H), 7.12 (d, J = 5.6 Hz, 1H), 6.57 (s, 2H), 6.43 (s, 1H), 3.78 (s, 3H), 2.54–2.50 (m, 1H), 1.88–1.77 (m, 2H), 1.75 (s, 3H), 1.68–1.61 (m, 2H), 1.53–1.49 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 160.1, 144.7, 142.8, 140.0, 131.8, 127.4, 126.9, 126.1, 108.3, 99.2, 88.9, 84.4, 70.1, 55.4 (3C), 55.3, 33.6, 33.5, 33.0, 30.2, 25.0.
3. Experimental Procedures for the Pt-Catalyzed Casacade

General procedure

To a solution of propargyl alcohol biaryl (0.1 mmol, 1 equiv) in toluene (2 mL) PtCl$_2$ (0.01 mmol, 10 mol %) was added. The mixture was sealed carefully and stirred at 80 °C under N$_2$ until TLC showed complete substrate conversion. The reaction mixture was filtered through a plug of celite and washed with EtOAc. The filtrate was concentrated, and the residue was purified using column chromatography on silica gel.

10-(Cyclopentylidenemethyl)-1,3-dimethoxyphenanthrene (4a). Following the general procedure, phenanthrene 4a was obtained as a white solid (29.4 mg, 96% yield). m.p. 80–84 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.53–8.51 (m, 1H), 7.78–7.76 (m, 1H), 7.71 (d, J = 1.5 Hz, 1H), 7.54 (dd, J = 6.0 Hz, 3.3 Hz, 2H), 7.43 (s, 1H), 7.12 (s, 1H), 6.68 (d, J = 1.7 Hz, 1H), 4.00 (s, 3H), 3.89 (s, 3H), 2.55 (t, J = 6.7 Hz, 2H), 2.43 (t, J = 6.1 Hz, 2H), 1.78–1.67 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.4, 158.3, 141.9, 134.3, 133.6, 132.3, 128.6, 127.9, 126.7, 125.4 (2C), 124.2, 122.9, 118.0, 99.5, 96.4, 56.1, 55.3, 34.2, 30.3, 26.7, 25.9; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3052, 2999, 2950, 2868, 2835, 1612, 1455, 1275, 1206, 1164, 790, 749; HRMS (FAB): calcd. for C$_{22}$H$_{22}$O$_2$ [M$^+$] 318.1620, found 318.1624.

10-(But-1-en-1-yl)-1,3-dimethoxyphenanthrene (4b). Following the general procedure, phenanthrene 4b was obtained as a yellow solid (14.7 mg, 97% yield,
cis:trans = 3:1). m.p. 86–89 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.54–8.49 (m, 1.3H), 7.81–7.77 (m, 1.3H), 7.70 (d, \(J = 1.8\) Hz, 1.3H), 7.58–7.51 (m, 2.6H), 7.50 (s, 0.3H), 7.41 (d, \(J = 15.4\) Hz, 0.3H), 7.33 (s, 1H), 7.12 (d, \(J = 11.3\) Hz, 1H), 6.67 (d, \(J = 1.9\) Hz, 1.3H), 5.98 (td, \(J = 15.3\) Hz, 0.3H), 5.61 (td, \(J = 11.4\) Hz, 7.4 Hz, 1H), 4.01 (s, 3.9H), 3.92 (s, 0.9H), 3.88 (s, 3H), 2.31 (pentet, \(J = 7.3\) Hz, 0.6H), 2.21 (pentet, \(J = 7.4\) Hz, 2H), 1.18 (t, \(J = 7.4\) Hz, 0.9H), 1.02 (t, \(J = 7.5\) Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 159.3, 159.2, 158.5, 158.4, 135.2, 133.6, 133.5, 133.2, 132.5, 132.51, 132.46, 132.1, 131.0, 129.3, 129.1, 128.9, 128.2, 126.7, 125.9, 125.7, 125.6, 124.1, 123.0, 118.1, 117.5, 99.4, 99.2, 96.4, 55.9, 55.8, 55.38, 55.35, 25.9, 21.5, 14.7, 13.8; IR (neat, cm\textsuperscript{-1}) \(\nu_{\text{max}}\) 3002, 2962, 2935, 2873, 2836, 1614, 1595, 1457, 1276, 1206, 1164, 1026, 749; HRMS (FAB): calcd. for C\textsubscript{20}H\textsubscript{20}O\textsubscript{2} \([M]^+\) 292.1463, found 292.1471.

\textit{tert-Butyl(5-(6,8-dimethoxyphenanthren-9-yl)pent-4-en-1-yl)oxy}dimethylsilane (4c). Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 20:1), to afford the desired product 4c as a yellow oil (41 mg, 95%, \(Z:E = 3:1\)). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.53–8.48 (m, 1.3H), 7.80–7.75 (m, 1.3H), 7.69–7.67 (m, 1.3H), 7.56–7.53 (m, 2.6H), 7.48 (d, \(J = 12.3\) Hz, 0.6H), 7.41 (d, \(J = 15.3\) Hz, 0.3H), 7.31 (s, 1H), 7.14 (d, \(J = 11.3\) Hz, 1H), 6.67–6.66 (m, 1.3H), 5.92 (td, \(J = 15.6\) Hz, 7.9 Hz, 0.3H), 5.61 (td, \(J = 13.4\) Hz, 5.7 Hz, 1H), 4.00 (s, 3.9H), 3.92 (s, 0.9H), 3.87 (s, 3H), 3.74 (t, \(J = 6.6\) Hz, 0.6H), 3.54 (t, \(J = 8.8\) Hz, 2H), 2.33 (q, \(J = 7.3\) Hz, 0.6H), 2.23 (q, \(J = 7.3\) Hz, 2H), 1.79 (quintet, \(J = 7.6\) Hz, 0.6H), 1.63 (quintet, \(J = 7.1\) Hz, 2H), 0.92 (s, 3H), 0.79 (s, 9H), 0.60 (s, 1.8H), –0.05 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 159.3, 159.2, 158.5, 135.1, 134.5, 133.6, 133.5, 133.4, 132.5, 132.4, 132.1, 129.1, 129.0, 128.9, 128.2, 127.0, 126.8, 126.7, 126.0, 125.72, 125.62, 124.2, 122.9, 118.0, 117.5, 99.3, 99.2, 96.3, 62.93, 62.87, 55.8, 55.4, 33.4, 32.8, 29.2, 26.00, 25.88, 24.5, 18.4, 18.3, –5.2, –5.3; IR (CHCl\textsubscript{3}, cm\textsuperscript{-1}) \(\nu_{\text{max}}\) 2953, 2929, 2857, 1613, 1461, 1205, 1103, 942, 834, 746; HRMS (FAB): calcd. for C\textsubscript{27}H\textsubscript{36}O\textsubscript{3}Si \([M]^+\) 436.2434, found 436.2436.
2-((5-(6,8-Dimethoxyphenanthren-9-yl)pent-4-en-1-yl)isoindoline-1,3-dione (4d). Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 15:1), to afford the desired product 4d as a light brown solid (41.1 mg, 91%, Z:E = 4:1). m.p. 114–115 °C; 1H NMR (400 MHz, CDCl3) δ 8.50–8.48 (m, 1.25H), 7.83–7.82 (m, 0.5H), 7.77–7.75 (m, 1.25H), 7.75–7.73 (m, 2H), 7.67–7.65 (m, 1.75H), 7.63–7.61 (m, 2H), 7.56–7.51 (m, 2.5H), 7.44 (d, J = 15.0 Hz, 0.25H), 7.44 (s, 0.25H), 7.28 (s, 1H), 7.17 (d, J = 11.3 Hz, 1H), 6.67 (s, 0.25H), 6.64 (d, J = 1.5 Hz, 1H), 5.90 (td, J = 15.3 Hz, 7.6 Hz, 0.25H), 5.63 (td, J = 11.3 Hz, 7.4 Hz, 1H), 3.99 (s, 3.75H), 3.91 (s, 0.75H), 3.88 (s, 3H), 3.82 (t, J = 7.3 Hz, 0.5H), 3.59 (t, J = 7.6 Hz, 2H), 2.36 (q, J = 7.1 Hz, 0.5H), 2.27 (q, J = 7.3 Hz, 2H), 1.96 (quintet, J = 7.3 Hz, 0.5H), 1.78 (quintet, J = 7.5 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 168.4, 168.3, 159.2, 158.6, 158.5, 135.2, 134.8, 134.4, 133.8, 133.7, 133.6, 133.4, 132.4, 132.2, 132.13, 132.09, 132.0, 129.1, 128.9, 128.3, 127.6, 126.8, 126.7, 125.9, 125.8, 125.6, 124.2, 123.1, 123.0, 122.9, 117.9, 99.1, 96.3, 55.8, 55.7, 55.4, 37.9, 37.6, 30.3, 28.9, 28.4, 25.5; IR (CHCl3, cm⁻¹) νmax 2940, 2838, 1771, 1710, 1613, 1397, 1277, 1025, 944, 719; HRMS (FAB): calcd. for C29H25NO4 [M]+ 451.1784, found 451.1795.

Methyl 5-(6,8-dimethoxyphenanthren-9-yl)pent-4-enoate (4f).

Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 5:1), to afford the desired product 4f as a light yellow solid (22.0 mg, 87%, Z:E = 3:1). m.p. 65–70 °C; 1H NMR (400 MHz, CDCl3) δ 8.53–8.48 (m, 1.3H), 7.79–7.77 (m, 1.3H), 7.68 (s, 1.3H), 7.58–7.53 (m, 2.6H), 7.47 (s, 0.3H), 7.45 (d, J = 14.6 Hz, 0.3H), 7.30 (s, 1H), 7.18 (d, J = 11.4 Hz, 1H), 6.65 (s, 1.3H), 5.89 (td, J = 15.4 Hz, 0.3H), 5.57 (td, J = 11.3 Hz, 7.2 Hz, 1H), 4.00 (s, 3.9H), 3.92 (s, 0.9H), 3.87 (s, 3H), 3.70 (s, 0.9H), 3.57 (s, 3H), 2.62–2.55 (m, 1.2H), 2.52 (q, J = 7.4 Hz, 2H), 2.38 (t, J = 7.4 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 173.7, 173.6, 159.2, 159.1, 159.1, 158.6, 158.5, 135.4, 134.7, 134.6, 133.6, 133.5, 132.4, 132.02, 131.98, 129.2, 129.0, 128.28, 128.26, 126.8, 125.9, 125.7, 124.8, 124.3, 123.0,
5-(6,8-Dimethoxyphenanthren-9-yl)pent-4-enoic acid (4e). Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 3:1), to afford the desired product 4e as a red solid (27.2 mg, 73%, Z:E = 1.5:1).

1,3-Dimethoxy-10-styrlyphenanthrene (4g). Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 10:1), to afford the desired product 4g as a yellow oil (28.3 mg, 83%, Z:E = 1:1). Compound 4g is rather unstable in solution. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.55–8.53 (m, 2H), 8.23 (d, $J$ = 15.8 Hz, 1H), 7.86–7.84 (m, 1H), 7.72 (dd, $J$ = 7.7 Hz, 2.1 Hz, 2H), 7.67 (s, 1H), 7.60–7.53 (m, 6H), 7.47 (t, $J$ = 7.1 Hz, 1H), 7.41–7.37 (m, 3H), 7.31–7.25 (m, 2H), 7.16 (dd, $J$ = 7.5 Hz, 1.2 Hz, 2H), 7.07–6.99 (m, 3H), 6.85 (d, $J$ = 15.8 Hz, 1H), 6.71 (t, $J$ = 2.6 Hz, 2H), 6.53 (d, $J$ = 12.0 Hz, 1H), 4.03 (s, 3H), 4.02 (s, 3H), 3.94 (s, 3H), 3.91 (s, 3H); $^{13}$C NMR (75 MHz, CDCl3) $\delta$ 159.2, 159.1, 158.7, 158.6, 138.5, 137.4, 134.9, 134.5, 133.71, 133.67, 133.6, 133.57, 133.67, 133.6, 132.7, 132.33, 132.29, 129.3, 129.1 (2C), 128.9, 128.6 (2C), 128.39, 128.36, 127.9 (2C), 127.7, 127.0, 126.9, 126.7, 126.4 (2C), 126.1, 125.95, 125.86 (2C), 125.3, 124.1, 123.0, 122.9, 117.8, 117.3, 99.2, 99.1, 96.39, 96.35, 56.1, 55.9, 55.41, 55.37; IR (CHCl$_3$, cm$^{-1}$) $\nu$$_{max}$ 3058, 3023, 3003, 2960, 2938, 2835, 1613, 1455, 1278, 1207, 1164, 1026, 750; HRMS (FAB): calcd. for C$_{24}$H$_{30}$O$_2$ [M]$^+$ 340.1463, found 340.1469.

1,3-Dimethoxy-10-(2-methylstyryl)phenanthrene (4h). Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 10:1), to afford the desired product 4h as a yellow solid (28.3 mg, 87%, Z:E = 9:1).
chromatography on silica gel (hexane/EtOAc, 10:1), to afford the desired product 4h as a light yellow solid (25.2 mg, 71%, Z:E = 1:1.4). Compound 4h is rather unstable in solution. m.p. 109–111 °C; 1H NMR (500 MHz, CDCl₃) δ 8.54–8.52 (m, 1.4H), 8.48 (d, J = 8.2 Hz, 1H), 8.11 (d, J = 15.7 Hz, 1.4H), 7.87–7.85 (m, 1.4H), 7.71–7.68 (m, 4H), 7.65 (s, 1.4H), 7.57–7.55 (m, 2.8H), 7.50–7.47 (m, 2H), 7.42–7.36 (m, 2H), 7.24–7.23 (m, 1H), 7.21–7.16 (m, 3H), 7.12 (s, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.01 (d, J = 15.7 Hz, 1.4H), 6.96–6.91 (m, 2H), 6.73–6.71 (m, 3.4H), 6.61 (d, J = 11.9 Hz, 1H), 4.02 (s, 7.2H), 3.95 (s, 7.2H), 2.48 (s, 4.2H), 2.35 (s, 3H); 13C NMR (125 MHz, CDCl₃) δ 159.23, 159.19, 158.7, 158.6, 137.4, 136.7, 136.2, 135.3, 135.0, 134.9, 133.6, 132.7, 132.4, 132.2, 130.4, 129.7, 129.4, 128.8, 128.45, 128.38, 126.9, 126.6, 126.4, 126.2, 126.1, 126.0, 125.8, 125.5, 125.3, 124.3, 124.1, 123.0, 122.8, 118.0, 117.5, 99.3, 99.0, 96.4, 96.3, 56.1, 55.4, 20.1, 20.0; IR (CHCl₃, cm⁻¹) υₘₐₓ 3601, 3006, 2940, 2835, 1614, 1457, 1207, 1164, 1026, 830, 749; HRMS (FAB): calcd. for C₂₅H₂₂O₂ [M]⁺ 354.1620, found 354.1618.

1,3-dimethoxy-10-(4-methylstyryl)phenanthrene (4i). Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 10:1), to afford the desired product 4i as a light yellow solid (23.0 mg, 65%, Z:E = 1:1.4). Compound 4i is rather unstable in solution. m.p. 125–129 °C; 1H NMR (400 MHz, CDCl₃) δ 8.54–8.52 (m, 2.4H), 8.18 (d, J = 15.8 Hz, 1.4H), 7.85 (d, J = 4.8 Hz, 1.4H), 7.71 (d, J = 8.5 Hz, 2.4H), 7.66 (s, 1.4H), 7.61–7.52 (m, 5H), 7.49–7.45 (m, 4H), 7.39 (s, 1H), 7.20–7.18 (m, 3.4H), 7.04 (d, J = 7.6 Hz, 2H) 6.85–6.80 (m, 3.4H), 6.70 (s, 2.4H), 6.49 (d, J = 12.0 Hz, 1H), 4.07 (s, 3H), 4.03 (s, 4.2H), 3.94 (s, 4.2H), 3.90 (s, 3H), 2.38 (s, 4.2H), 2.19 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 159.3, 159.2, 158.7, 158.6, 136.8, 135.8, 135.7, 134.7, 134.5, 134.1, 133.8, 133.6, 133.0, 132.7, 132.42, 132.38, 129.35, 129.3, 129.0, 128.7, 128.4, 128.2, 127.7, 126.9, 126.7, 126.3, 125.9, 125.8, 125.2, 124.0, 123.0, 122.9, 117.9, 117.5, 99.3, 99.2, 96.5, 96.4, 56.1, 56.0, 55.41, 55.37, 21.2, 21.0; IR (CHCl₃, cm⁻¹) υₘₐₓ 3058, 3010, 2958, 2937, 2834, 1612, 1455, 1276, 1205, 1163, 1025, 748; HRMS (FAB): calcd. for C₂₅H₂₂O₂ [M]⁺ 354.1620, found 354.1618.
1,3-dimethoxy-10-(2-(trifluoromethyl)styryl)phenanthrene (4j).

Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 10:1), to afford the desired product 4j as a light yellow solid (26.5 mg, 65%, Z:E = 1:3). Compound 4j is rather unstable in solution. m.p. 144–148 °C; 1H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.57–8.54 (m, 1H), 8.49 (d, J = 8.4 Hz, 0.3H), 8.19 (d, J = 15.6 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.89–7.87 (m, 1H), 7.72 (d, J = 2.2 Hz, 1H), 7.69 (d, J = 7.4 Hz, 1.3H), 7.65 (s, S20 1H), 7.63–7.56 (m, 3.6H), 7.53–7.47 (m, 0.9H), 7.43 (d, J = 7.8 Hz, 0.3H), 7.38 (t, J = 7.7 Hz, 1H), 7.15 (dd, J = 15.6 Hz, 2.5 Hz, 1H), 7.12–7.09 (m, 0.3H), 7.06–6.96 (m, 0.6H), 6.82 (dd, J = 11.8 Hz, 2.4 Hz, 0.3H), 6.75 (t, J = 2.4 Hz, 1.3H), 4.01 (s, 3.9H), 3.97 (s, 3.9H); 13C NMR (125 MHz, CD$_2$Cl$_2$) δ 159.6, 159.5, 138.4, 138.2 (d, J = 5.0 Hz, 1H), 134.7, 134.1, 132.84, 132.82 (d, J = 5.0 Hz, 1H), 132.80, 132.7, 132.5, 131.6, 130.1, 129.5, 129.2, 128.8, 127.9, 127.6, 127.2 (q, J = 38.8 Hz), 127.3, 126.9, 126.7 (d, J = 5.0 Hz), 126.4 (q, J = 5.0 Hz), 125.2 (q, J = 222.5 Hz), 125.0, 123.7, 123.6, 123.5, 122.6, 117.7, 100.0, 99.5, 97.1, 97.0, 56.7, 55.98, 55.96; IR (CHCl$_3$, cm$^{-1}$) $\nu_{max}$ 3071, 2961, 2936, 2875, 2727, 2614, 1456, 1314, 1207, 1160, 1120, 1035, 831, 765, 747; HRMS (FAB): calcd. for C$_{25}$H$_{19}$F$_3$O$_2$ [M]$^+$ 408.1337, found 408.1328.

6-(Cyclopentylidinemethyl)phenanthro[2,3-d][1,3]dioxole (4k). Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 15:1), to afford the desired product 4k as a light yellow solid (23.3 mg, 79%). m.p. 126–127.5 °C; 1H NMR (400 MHz, CDCl$_3$) δ 8.42 (d, J = 8.0 Hz, 1H), 8.04 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.53 (s, 1H), 7.51 (t, J = 6.6 Hz, 2H), 7.47 (s, 1H), 6.71 (s, 1H), 5.98 (s, 2H), 2.58 (t, J = 6.9 Hz, 2H), 2.40 (t, J = 7.1 Hz, 2H), 1.72 (hexet, J = 14.5 Hz, 7.2 Hz, 4H); 13C NMR (100 MHz, CDCl$_3$) δ 149.1, 147.6, 147.5, 134.3, 131.3, 129.3, 128.3, 127.8, 126.6, 125.73, 125.71, 124.9, 122.2, 118.3, 103.2, 101.3, 101.1, 34.5, 30.7, 26.6, 25.9; IR (neat, cm$^{-1}$) $\nu_{max}$ 2956, 2893, 2872, 2838, 1502, 1471, 1262, 1240, 1041, 745; HRMS
10-(Cyclopentylidenemethyl)-2,3,6-trimethoxyphenanthrene (4l). Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 10:1), to afford the desired product 4m as a yellow solid (33.5 mg, 92%). m.p. 139–142 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (s, 1H), 7.83 (s, 1H), 7.72 (d, $J = 8.7$ Hz, 1H), 7.50 (s, 1H), 7.41 (s, 1H), 7.16 (d, $J = 8.8$ Hz, 1H), 6.75 (s, 1H), 4.09 (s, 3H), 4.03 (s, 3H), 4.00 (s, 3H), 2.61 (t, $J = 6.4$ Hz, 2H), 2.44 (t, $J = 6.4$ Hz, 2H), 1.78–1.69 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 157.8, 149.0, 148.6, 148.5, 131.3, 130.0, 129.8, 126.7, 126.0, 124.4, 124.3, 117.9, 115.3, 105.6, 103.8, 103.6, 56.0, 55.8, 55.5, 34.5, 30.9, 26.6, 25.8; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 2998, 2955, 2868, 2833, 1702, 1618, 1523, 1506, 1268, 1207, 1162, 1036; HRMS (FAB): calcd. for C$_{21}$H$_{18}$O$_2$ [M+H]$^+$ 302.1307, found 302.1318.

10-(Cyclopentylidenemethyl)-3-methoxyphenanthrene (4m) and 10-(cyclopentylidenemethyl)-1-methoxyphenanthrene (4m'): Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc/acetone, 100:0.5:0.5), to afford the desired product 4n as a light yellow solid (51.3 mg, 61%) and 4n' as a yellow solid (10.3 mg, 12%).

10-(Cyclopentylidenemethyl)-3-methoxyphenanthrene (4m), a light yellow solid, m.p. 82.5–85 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.56 (d, $J = 7.5$ Hz, 1H), 8.07 (s, 1H), 8.04 (d, $J = 9.0$ Hz, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.58–7.52 (m, 2H), 7.51 (s, 1H), 7.22 (d, $J = 1.4$ Hz, 1H), 6.82 (s, 1H), 4.01 (s, 3H), 2.60 (t, $J = 6.6$ Hz, 2H), 2.43 (t, $J = 6.5$ Hz, 2H), 1.79–1.69 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 158.1, 149.0, 134.4, 132.4, 131.7, 129.0, 128.3, 126.9, 126.6, 126.0, 125.5, 124.0, 122.4, 118.0, 116.1, 104.3, 55.5, 34.6, 30.9, 26.6, 25.8; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3062, 3002, 2954, 2869, 2836, 1617, 1453, 1435, 1229, 1035, 746; HRMS (FAB):
10-(Cyclopentylidenemethyl)-1-methoxyphenanthrene (4m'). a yellow solid, m.p. 80–83 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.59 (d, \(J = 7.0\) Hz, 1H), 8.33 (d, \(J = 6.6\) Hz, 1H), 7.77 (d, \(J = 7.2\) Hz, 1H), 7.57–7.51 (m, 4H), 7.14 (s, 1H), 7.03 (d, \(J = 6.2\) Hz, 1H), 3.90 (s, 3H), 2.54 (t, \(J = 5.6\) Hz, 2H), 2.41 (t, \(J = 5.4\) Hz, 2H), 1.73 (q, \(J = 5.5\) Hz, 2H), 1.66 (q, \(J = 5.4\) Hz, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 158.3, 141.9, 134.3, 132.8, 131.9, 129.2, 127.9, 127.7, 126.7, 126.4, 125.9, 124.4, 123.0 (2C), 115.9, 109.0, 56.4, 34.2, 30.2, 26.7, 25.9; IR (CHCl\(_3\), cm\(^{-1}\)) \(\upsilon_{\text{max}}\) 3060, 3000, 2954, 2860, 1602, 1449, 1430, 1229, 1030, 734; HRMS (FAB): calcd. for \(\text{C}_{21}\text{H}_{20}\text{O}[M]^+\) 288.1514, found 288.1529.

10-(Cyclopentylidenemethyl)-1,3-dimethoxy-9-methylphenanthrene (4n). A mixture of the product did not be isolated. The ratio of desired and undesired products (4n and fluorene 8) formed was 1:1 in 80%. A remain 20% might be converted into another undesired or decomposed adducts. The yield and ratio were determined by \(^1\)H NMR with internal standard 1,1,2,2-tetrachloroethane.

4,10-Bis(cyclopentylidenemethyl)-1,3-dimethoxypyrene (4q). a white solid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (s, 2H), 7.65 (s, 2H), 7.22 (s, 1H), 7.14(s, 1H), 2.59 (t, \(J = 5.0\) Hz, 4H), 2.48 (d, \(J = 4.7\) Hz, 4H), 1.79–1.68 (m, 8H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.6 (2C), 142.1 (2C), 134.9, 132.0, 126.3, 126.0 (2C), 124.5 (2C),122.4 (2C), 57.5 (2C), 34.3 (2C), 30.2 (2C), 26.7 (2C), 26.0 (2C).
9-(Cyclopentylethynyl)-1,3-dimethoxy-9H-fluorene (5a). To a solution of propargyl alcohol biaryl 1a (33.6 mg, 0.1 mmol) in toluene (2 mL), InCl₃ (2.2 mg, 0.01 mmol) was added. The mixture was sealed carefully and stirred at 80 °C for 2 h under N₂ until TLC showed complete substrate conversion. The reaction mixture was filtered through a plug of celite and washed with EtOAc. The filtrate was concentrated, and the residue was purified using column chromatography on silica gel (hexane/EtOAc, 20:1) to give a fluorene 5a as a yellow oil (24.8 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (t, J = 6.9 Hz, 2H), 7.37–7.30 (m, 2H), 6.86 (s, 1H), 6.44 (s, 1H), 4.69 (s, 1H), 3.92 (s, 1H), 3.88 (s, 3H), 2.59–2.56 (m, 1H), 1.88–1.78 (m, 2H), 1.72–1.63 (m, 2H), 1.56–1.50 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 157.3, 145.8, 142.6, 140.2, 127.5, 127.3, 125.0, 123.8, 119.9, 98.5, 96.5, 85.6, 76.4, 55.7, 36.9, 34.0 (2C), 30.5, 24.8 (2C); IR (neat, cm⁻¹) υ max 3055, 3000, 2958, 2871, 2840, 1703, 1608, 1592, 1350, 1206, 1156, 938, 765; HRMS (FAB): calcd. for C₂₀H₂₂O₂ [M⁺] 318.1620, found 318.1628.

2-(Benzylxy)-5,6-diphenyl-5,6-dihydronaphtho[3,2,1-de]chromene (6b). Following the general procedure, the crude product was purified using column chromatography on silica gel (hexane/EtOAc, 30:1), to afford the desired product 6b as a light yellow solid (21.5 mg, 71%). m.p. 202–205 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, J = 8.0 Hz, 1H), 7.90 (s, 1H), 7.73 (d, J = 7.4 Hz, 1H), 7.61–7.51 (m, 4H), 7.47–7.40 (m, 3H), 7.36 (d, J = 7.2 Hz, 1H), 7.32 (s, 1H), 7.22 (s, 2H), 7.13–7.11 (m, 2H), 7.05–7.03 (m, 2H), 6.98 (t, J = 7.2 Hz, 2H), 6.6 (d, J = 7.3 Hz, 2H), 5.62 (s, 1H), 5.30 (s, 2H), 4.52 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 158.6, 155.6, 139.1, 138.8, 136.9, 132.7, 132.4, 132.1, 129.3 (2C), 129.1, 128.7 (2C), 128.4, 128.1, 127.9 (2C), 127.7 (2C), 127.6 (2C), 127.5, 127.0, 126.5, 126.4 (2C), 125.9, 123.1, 121.9, 114.8, 102.6, 100.2, 81.2, 70.4, 52.0; IR (neat cm⁻¹) υ max 3065, 3032, 2909, 2873, 1618, 1454, 1284, 1159, 1139, 751, 698; HRMS (FAB): calcd. for C₃₅H₂₆O₂ [M⁺] 478.1933, found 478.1939.
Scheme S-7. Oxidation of diastereomeric mixture 6b to confirm its chemical structure

\[ \text{Scheme S-7.} \]

2-(Benzylxy)-5,6-diphenylnaphto[3,2,1-de]chromene. To a solution of 6b (20.0 mg, 0.042 mmol) in benzene (1 mL), DDQ (16.1 mg, 0.071 mmol) was added. The mixture was sealed carefully and stirred at room temperature overnight under N₂ until TLC showed complete substrate conversion. The reaction mixture was diluted with DCM and extracted with sat. NaHCO₃ and brine twice. The organic layer was concentrated, and the residue was purified using column chromatography on silica gel (hexane/EtOAc, 30:1) to give the product as a yellow solid (16.4 mg, 82% yield). m.p. 153–155 °C; \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 8.29–8.27 (m, 1H), 7.66 (s, 1H), 7.52 (d, \(J = 7.4\) Hz, 2H), 7.49–7.47 (m, 1H), 7.43–7.33 (m, 8H), 7.31–7.27 (m, 4H), 7.19–7.17 (m, 3H), 6.86 (s, 1H), 6.55 (s, 1H), 5.24 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 158.9, 153.5, 148.8, 136.8, 135.6, 134.2, 133.9, 132.7, 131.2 (2C), 129.4, 129.00 (2C), 128.97 (2C), 128.7 (2C), 128.5, 128.4, 128.1 (2C), 127.9, 127.7 (2C), 127.5 (2C), 127.3, 125.2, 122.8, 117.6, 115.3, 113.7, 100.7, 100.0, 70.4; IR (neat, cm⁻¹) \(\nu_{max}\) 3061, 3032, 2925, 2925, 1638, 1612, 1408, 1215, 1162, 840, 746, 697; HRMS (FAB): calcd. for C₃₅H₂₄O₂ [M⁺] 476.1776, found 476.1777.
VI. References


(7) See the Supporting Information for synthesis details.


(9) The ratio of Z/E isomer was not significantly changed when the catalyst, solvent, and reaction time were varied.

(10) The substrate 4e showed slightly lower Z/E selectivity than other primary alkyl group
substituted derivatives.


