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Gold-Catalyzed Oxidation Terminal Alkyne: An Approach to Synthesize Substituted Dihydronaphthalen-2(1*H*)-ones and Phenanthrenols

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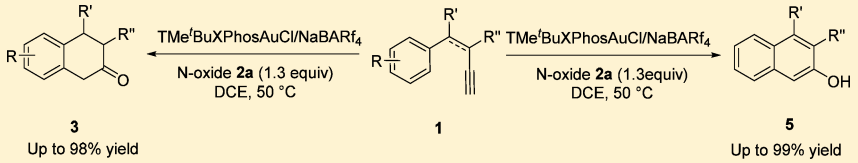
Supporting Information



ABSTRACT: A facile gold-catalyzed oxidation terminal alkynes to synthesize substituted dihydronaphthalen-2(1*H*)-ones **3** and phenanthrenols **5** was realized. Various useful structures and drug precursors were generated in up to 99% yield under mild condition and low catalyst loading.

Aromatic rings are "privileged structures" and important motifs in natural products and biologically active molecules. A number of aromatic systems, such as tetrahydronaphthalene and phenanthrene analogues, possessing interesting biological properties were reported. They are also potentially useful precursors for drug discovery programs and functional group transformations (Figure 1).[1] In this context,

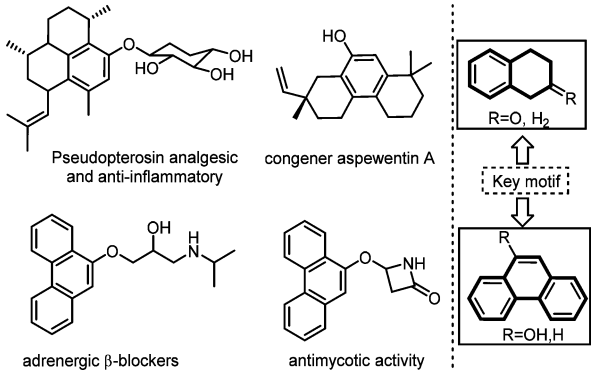


Figure 1. Examples of bioactive structures.

the development of useful methods to synthesize functionalized tetrahydronaphthalene and phenanthrene derivatives with safe and simple conditions continues to be actively pursued.

Recently, gold(I)-catalyzed oxidation of alkynes using pyridine/quinoline N-oxides as oxidants to synthesize various useful molecules was reported.[2] The α-oxo gold carbene intermediates generated from alkynes can be trapped in situ by internal/external nucleophiles,[3−5] which circumvents the use of hazardous and potentially explosive α-diazo ketone precursors.[6,7] Terminal alkynes as the research object are also widely studied and the generated α-oxo gold carbene intermediates are trapped in situ by relatively electron-rich nucleophiles, such as oxygen,[8] nitrogen,[9] sulfur,[10] electron-rich aryl ether,[11] C−C double and triple bonds.[12] Recently, Zhang and co-workers reported the gold catalyzed oxidation of propargyl aryl ethers to synthesize chroman-3-ones by using internal *ortho*-carbon of aryl ether as nucleophiles to trap the in situ generated α-oxo gold carbenes.[11] In contrast, the use of an unactivated aryl sp^2 carbon to trap the highly reactive α-oxo gold carbene intermediates efficiently proved to be challenging because of the double oxidation of terminal alkynes and other intractable side reactions.[13] Thus, reports on the successful use of aryl sp^2 carbon to trap the α-oxo gold carbene generated in situ from terminal alkynes are limited. In 2013, Gagosz and co-workers reported gold catalyzed oxidative cyclization of propynyl arenes into indan-2-ones by using aryl sp^2 carbon as nucleophiles, which suggested a S_N2'-type process.[14] To further develop terminal alkynes as surrogates of hazardous α-diazo ketones in gold(I) catalysis, we focused here on expanding the scope of suitable internal nucleophiles, such as aryl groups. Our first target was flexible aryl-substituted alkyne **1**, as shown in Scheme 1C, our design anticipated that a terminal α-oxo gold carbene could be generated upon oxidation of the terminal C−C triple bond, which was then trapped by aryl group. Gagosz and co-workers have reported three examples of this type of C−H functionalization using 3-butynylbenzene substrate in the presence of methanesulfonic acid and bulky pyridine N-oxides with the products overall yield less than 45%.[14] We surmised

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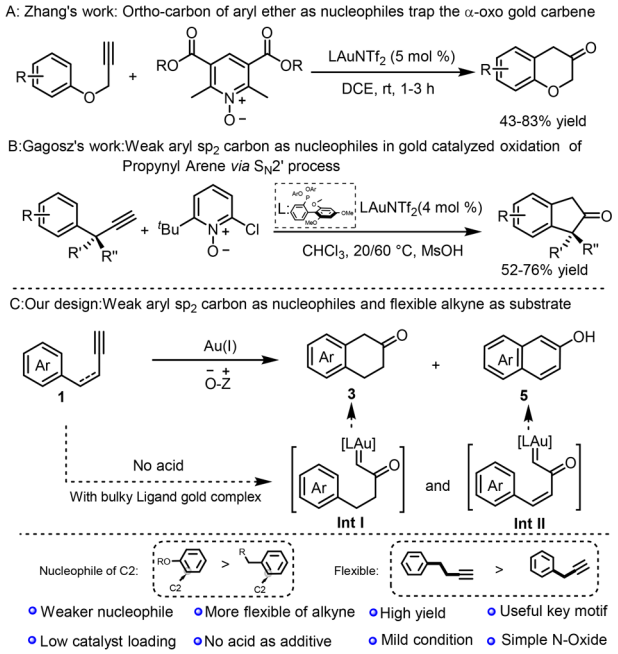
Scheme 1. Background and Our Design

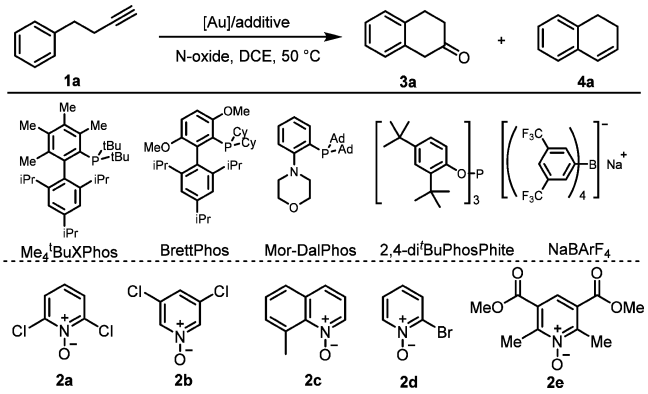


that this strategy, if realized with more flexible alkynes, would offer rapid access to synthetically versatile dihydronaphthalen-2(1*H*)-ones **3** and phenanthrenols **5** under mild conditions in the absence of acid as an additive (Scheme 1).

The commercially available 3-butyn-1-ylbenzene, **1a**, was chosen as a model substrate to determine the catalytic conditions leading to the corresponding 3, 4-dihydronaphthalen-2(1*H*)-one **3a**. The reaction optimization results are shown in Table 1. Initially, the substrate **1a** was treated with $Me_4{}^tBuXPhosAuCl$ (2 mol%)/$NaBARF_4$ (3 mol%) and 1.2 equiv of pyridine oxides (**2a**−**e**). The reactions were carried out at 50 °C in 1,2-dichloroethane (DCE) and monitored by ^1H NMR spectroscopy for 5 h. To our delight, it was observed that **1a** was converted to the corresponding **3a** in 83% yield with 2,6-dichloropyridine 1-oxide **2a** as the oxidant (entry 1). Other N-oxides, such as **2b**−**2d**, were inefficient even after longer times (entries 2−4). Notably, Zhang and co-workers recently reported that Hantzsch esters N-oxide **2e** is the best oxidant for promoting the cyclizations of propargyl aryl ethers to chroman-3-ones selectively, however, no superior result was observed in our case (entry 5). Different counteranions generated from silver salts, like $AgNTf_2$ and AgOTf, were both inefficient (entries 6−7). The effect of the solvents, like toluene and THF, were also considered, but no better results were observed (entries 8−9). Other cationic gold complexes derived from typical ligands, such as Ph_3P, Mor-dalPhos, IPr, and phosphite, were largely ineffective, thus resulting in 3-butyn-1-ylbenzene, **1a**, with little desired product (entries 10−14). In these reactions, only trace amounts of the 1,2-dihydronaphthalene **4a** was formed through a gold-catalyzed 6-*endo-dig* cyclization in the absence of the oxidant **2a**.

With $Me_4{}^tBuXPhosAuCl$ (2 mol%)/$NaBARF_4$ (3 mol%) as the catalyst system and pyridine 1-oxide **2a** as the oxidant, the scope of the transformation was first examined with various 3-butyn-1-ylbenzenes, as shown in Table 2. For the *para*-electron-donating substitution on the benzene ring, like methoxy, benzoxy, and allyloxy, reacted smoothly to give corresponding products in good to excellent yields (**3b**−**d**). More methoxy

Table 1. Screening Conditions.[a]



entry	N-oxide (equiv)	catalyst additive(mol%)	yield of **3a** and **4a** (%)[b]	
1	**2a** (1.2)	$Me_4{}^tBuXPhosAuCl(2)+NaBArF_4(3)$	83[c]	<2
2	**2b** (1.2)	$Me_4{}^tBuXPhosAuCl(2)+NaBArF_4(3)$	<3	<2
3	**2c** (1.2)	$Me_4{}^tBuXPhosAuCl(2)+NaBArF_4(3)$	30	<2
4	**2d** (1.2)	$Me_4{}^tBuXPhosAuCl(2)+NaBArF_4(3)$	<5	<2
5	**2e** (1.2)	$Me_4{}^tBuXPhosAuCl(2)+NaBArF_4(3)$	53	<2
6	**2a** (1.2)	$Me_4{}^tBuXPhosAuCl(2)+AgNTf_2(3)$	43	<2
7	**2a** (1.2)	$Me_4{}^tBuXPhosAuCl(2)+AgOTf(3)$	18	<2
8	**2a** (1.2)	$Me_4{}^tBuXPhosAuCl(2)+NaBArF_4(3)$	NR[d]	<2
9	**2a** (1.2)	$Me_4{}^tBuXPhosAuCl(2)+NaBArF_4(3)$	16[e]	<2
10	**2a** (1.2)	$PPh_3AuCl(2)+NaBArF_4(3)$	NR	NR
11	**2a** (1.2)	$BrettPhosAuCl(2)+NaBArF_4(3)$	15	<2
12	**2a** (1.2)	$Mor\text{-}DalPhosAuNTf_2(2)$	<3	
13	**2a** (1.2)	$IPrAuCl(2)+NaBArF_4(3)$	<3	
14	**2a** (1.2)	2,4-di-tBuPhosPhiteAuCl(2)+$NaBArF_4(3)$	NR	NR

[a][**1a**] = 0.05m, and 1.2 equiv of the oxidant. [b]Estimated by ^1H NMR spectroscopy using diethyl phthalate as the internal reference. [c]Yield of isolated product: 83%. [d]THF as solvent. [e]Toluene as solvent. DCE = 1,2-dichloroethane. THF = tetrahydrofuran.

substitutions on the benzene ring, like **1e**−**f**, were also tested, and the desired products overall yields were mostly less than 25%, along with 6-*endo-dig* cyclization products **4e**−**f**. In these cases, in the absence of the oxidant **2a**, a gold-catalyzed 6-*endo-dig* cyclization was facile, which suggested that electron rich substitution on the benzene ring played the requisite role of accelerating this side reaction. For this, 1.5 equiv of MsOH was added and the proton was coordinated with the methoxy substitutions, which reduced the electron on the benzene ring. Fortunately, substrate **1e** was smoothly converted to the desired product **3e** in 62% yields. To our delight, 2.0 equiv of MsOH was used in transforming **1f**, an excellent yield of **3f** (98% yield) was obtained. With an electron-withdrawing group, like **1g**, the reaction worked well and an accepted yield of corresponding product **3g** was obtained. The functional group tolerance of this chemistry is good as substrates with aliphatic R_2 group, methyl group (**1h**), and aliphatic ring group (**1i**) reacted well. Substrates 1-(but-3-yn-1-yl)naphthalene **1j**−**k** were readily tolerated and the desired products **3j**−**k** were obtained in an excellent yield.

While considering synthetically useful transformations and expanding the scope of this reaction, we examined the direct conversion of *o*-ethynyl-1,1′-biaryls **1aa**−**1ag** in the presence of $Me_4tBuXPhosAuCl$ (2 mol%)/$NaBARF_4$ (3 mol%)/**2a** system. Much to our delight, this strategy worked well with different R group substituents, thus affording various functionalized

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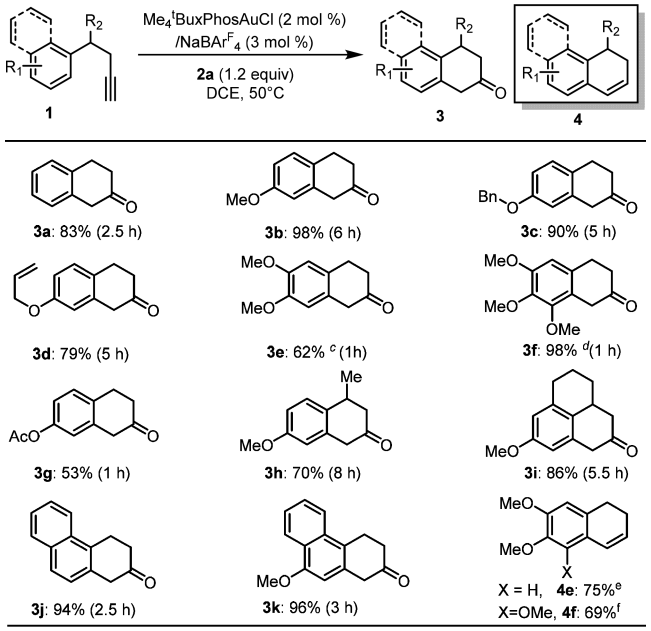
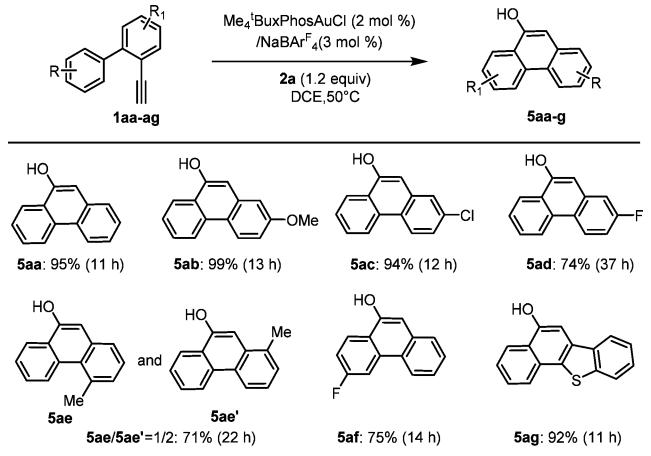
Table 2. Gold-Catalyzed Oxidation Terminal Alkynes To Synthesize Substituted Dihydronaphthalen-2(1*H*)-ones[a,b]



[a]The reactions were run in a vial without exclusion of air and moisture, and the substrate concentration was 0.05 M. [b]Yields of isolated products are reported. [c]1.5 equiv MsOH was added in standard condition. [d]2.0 equiv MsOH was added in standard condition. [e]The reaction was run in the absence of **2a** at 60 °C. [f]The reaction was run in the absence of **2a** at 40 °C.

phenanthrenols **5aa**−**5ad** in good to excellent yield as shown in Table 3. For the substrate **1ae**, by installing a methyl group on

Table 3. Gold-Catalyzed Oxidation Terminal Alkynes To Synthesize Substituted Phenanthrenols[a,b]

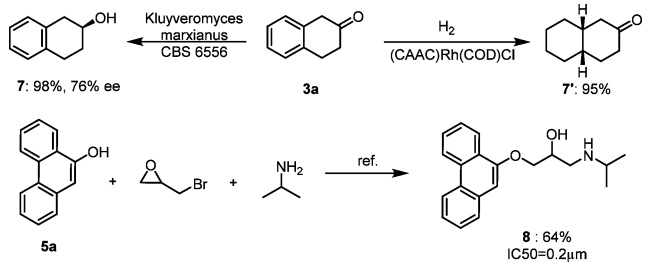


[a]The reactions were run in a vial without exclusion of air and moisture, and the substrate concentration was 0.05 M. [b]Yields of isolated products are reported.

mata position, the regioselectivity in this case was 2:1. Other *o*-ethynyl-1,1′-biaryl, such as **1af**, with an electron-withdrawing R′ group worked well to give the corresponding phenanthrenol **5af** in good yields. The substrate **1ag** with a benzo[*b*]thiophene R group can also afford the desired product **2ag** in 92% yield. In these reactions, no gold-catalyzed 6-*endo-dig* cyclization products were observed which is shown as excellent selectivity.[15]

For the products **3a** and **5a**, the motifs can be easily transferred to useful structure and drug molecular, as shown in Scheme 2.[16]

Scheme 2. Application of 3,4-Dihydronaphthalen-2(1*H*)-one 3a and Phenanthrenol 5a



In summary, we have described an efficient approach to synthesize substituted dihydronaphthalen-2(1*H*)-ones **3** and phenanthrenols **5** via gold-catalyzed oxidation terminal alkyne in low catalyst loading. The reaction proceeded smoothly to provide the corresponding products dihydronaphthalen-2(1*H*)-ones **3** in good to excellent yield. Phenanthrenols **5** were obtained smoothly in good yield and both electron-withdrawing and electron-donating substitutions were tolerated. Based on our developed method, various useful aromatic structures and drug precursors were synthesized under mild condition.

EXPERIMENTAL SECTION

General Information. Ethyl acetate (ACS grade), hexanes (ACS grade), diethyl ether (ACS grade) and anhydrous 1, 2-dichloroethane (anhydride, 99.8%) were purchased from Fisher Scientific and used without further purification. Methylene chloride and tetrahydrofuran were purified using MBraun Solvent Purifier. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Sorbent Technologies' precoated silica gel plates. Flash column chromatography was performed over Sorbent Technologies silica gel (230−400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 500 MHz spectrometers using residue solvent peaks as internal standards. Mass spectra were recorded with Micromass $QTOF_2$ Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization or Waters GCT Premier time-of-flight mass spectrometer with a field ionization (FI) ion source. Chemical shifts are reported in ppm with the internal chloroform signal at 7.26 and 77.0 ppm as a standard.

General Procedure A. Methods for the synthesis 3-butyn-1-ylbenzene derivatives **1a**−**k**. Step 1: A well-stirred solution of the aluminum (405 mg, 15 mmol, 1.5 equiv) and Hg_2Cl_2 (30 mg, 0.06 mmol, 6 mol%) in THF (10 mL) heated to 60−70 °C. The 3-bromoprop-1-yne (1.78 g, 15 mmol, 1.5 equiv) diluted by THF(10 mL) was added dropwise via syringe and the reaction was stirred at room temperature for 30 min under nitrogen atmosphere. The resulting mixture was then added dropwise to the solution of arylaldehyde (10 mmol, 1.0 equiv) in THF (10 mL) at −78 °C. The reaction was stirred under N_2 until substrate disappeared as judged by TLC, and then quenched with sat aq. NH_4Cl. The solution was washed with brine solution and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel using petroleum ether/EtOAc (20:1) as the eluent to afford 3-butyn-1-ylbenzene derivatives in 96% yield.

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Step 2: To a solution of 3-butyn-1-ylbenzene derivatives (9 mmol, 1.0 equiv) in DCM (27 mL) at 0 °C under N_2 atmosphere was added Et_3SiH (18 mmol, 2.09 g, 2.0 equiv), the reaction was stirred at this temperature for 30 min and then TFA or $BF_3{\cdot}Et_2O$ (36 mmol, 4.10g, 4.0 equiv) was added dropwise via syringe. The mixture was slowly warmed to room temperature and stirred until substrate disappeared, and quenched with sat aq. $NaHCO_3$. The solution was washed with brine solution and extracted with DCM (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product purified by chromotagraphy on silica gel using petroleum ether/EtOAc (15:1) as the eluent to affords product **1a**–**k** in 85% yield.

General Procedure B. Methods for the synthesis 2-ethynyl-1,1′-biphenyl derivatives **1aa**–**1ag**. Step 1: To a solution of $Pd(OAc)_2$ (0.3 mml, 67.2 mg, 0.03 equiv) and Na_2CO_3 (20 mmol, 1.68 g, 2.0 equiv) in 20 mL DMF/H_2O (2:1) was added phenylboronic acid (10.5 mmol, 1.28 g, 1.05 equiv), and the resulting mixture was stirred for 15 min. To this solution was added 2-bromobenzaldehyde (10 mmol, 1.85g, 1.0 equiv) at 0 °C, which was stirred for 3 h at room temperature. Quenched by Ammoium chloride solution, the solution was washed with brine solution and extracted with diethyl ether (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel using petroleum ether/EtOAc (40:1) as the eluent affording [1,1′-biphenyl]-2-carbaldehyde in 87% yield.

Step 2: To a solution of [1,1′-biphenyl]-2-carbaldehyde (8.7 mmol, 1.58 g, 1.0 equiv) and in CBr_4 (13.1 mmol, 4.3 g, 1.5 equiv) in anhydrous DCM (20 mL) cooled to 0 °C (ice–water bath) was added PPh_3 (26.1 mmol, 6.8 g, 3.0 equiv) as a solid in small portions. The light-yellow reaction mixture was then stirred at ambient temperature for 3–5 h. Solvent was removed in vacuo, and the residure was dissolved in petroleum ether/EtOAc (60:1). Triphenylphosphine oxide was filtered off by suction. The filtrate was concentrated under reduced pressure, and the crude gem-dibromide was purified by chromatography on silica gel using petroleum ether/EtOAc (40:1) as the eluent affording the product of gem-dibromide in 95% yield. A well-stirred solution of the gem-dibromide (8.3 mmol, 1.0 equiv) in anhydrous THF (20 mL) was cooled to −40 °C under an argon atmosphere, *n*-BuLi (2.5 M in hexane, 6.84 mL, 2.05 equiv) was then added dropwise via syringe. The stirring was continued at −40 °C until the reaction was complete as monitored by TLC. After completion of the reaction, the resultant light-yellow/orange mixture was diluted with distilled water, and the stirring was continued for 0.5 h to allow the mixture to slowly reach room temperature. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel using petroleum ether/EtOAc (40:1) as the eluent to afford the products **1aa**–**1ag** in 96% yield.

*3-Butyn-1-ylbenzene (**1a**).*[17] **1a** is a commercially available product.

*1-(But-3-yn-1-yl)-4-methoxybenzene (**1b**).* **1b** is a known compound.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, J = 8.6 Hz, 2H), 6.83 (t, J = 9.1 Hz, 2H), 3.79 (s, 3H), 2.79 (t, J = 7.5 Hz, 2H), 2.55–2.40 (m, 2H), 2.10–1.84 (m, 1H).

*1-(Benzyloxy)-4-(but-3-yn-1-yl)benzene (**1c**).* **1c** was prepared in 78% yield (1.84 g) through the General Procedure A.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.44–7.38 (m, 2H), 7.37–7.33 (m, 1H), 7.19–7.14 (m, 2H), 7.01–6.89 (m, 2H), 5.07 (s, 2H), 2.82 (t, J = 7.5 Hz, 2H), 2.53–2.43 (m, 2H), 2.01 (t, J = 2.6 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 137.1, 132.8, 129.4, 128.5, 127.9, 127.4, 114.8, 83.9, 70.0, 68.8, 34.0, 20.8, 6.8, 6.4. HRMS (ESI) m/z calcd for $C_{17}H_{17}O^+$ $(M+H)^+$: 237.1274, found 237.1274. GCMS (m/z): 236.12

*1-(Allyloxy)-4-(but-3-yn-1-yl)benzene (**1d**).* **1d** was prepared in 82% yield (1.53 g) through the General Procedure A.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19–7.09 (m, 2H), 6.97–6.80 (m, 2H), 6.08 (ddt, J = 17.2, 10.5, 5.3 Hz, 1H), 5.43 (ddd, J = 17.3, 3.2, 1.6 Hz, 1H), 5.35–5.23 (m, 1H), 4.53 (dt, J = 5.3, 1.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H), 2.53–2.40 (m, 2H), 2.00 (t, J = 2.6 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 133.4, 132.8, 129.3, 117.5, 114.7, 83.9, 68.8, 68.8, 34.0, 20.8. HRMS $(M+H)^+$ calcd for $C_{13}H_{15}O^+$: 187.1117, found 187.1117.

*4-(But-3-yn-1-yl)-1,2-dimethoxybenzene (**1e**).* **1e** is a known compound.[19] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93–6.64 (m, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 2.80 (t, J = 7.5 Hz, 2H), 2.47 (td, J = 7.5, 2.6 Hz, 2H), 1.98 (t, J = 2.6 Hz, 1H).

*5-(But-3-yn-1-yl)-1,2,3-trimethoxybenzene (**1f**).* **1f** is a known compound.[20] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.46 (s, 2H), 3.85 (s, 5H), 3.83 (s, 3H), 2.79 (t, J = 7.5 Hz, 2H), 2.48 (td, J = 7.5, 2.6 Hz, 2H), 2.09–1.77 (m, 1H).

*4-(But-3-yn-1-yl)phenyl acetate (**1g**).* **1g** was prepared in 73% yield (1.37 g) through the General Procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 2.84 (t, J = 7.5 Hz, 2H), 2.48 (td, J = 7.5, 2.6 Hz, 2H), 2.29 (s, 3H), 1.99 (t, J = 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 149.1, 137.9, 129.3, 121.4, 83.5, 69.0, 34.2, 21.1, 20.4. HRMS (ESI) m/z calcd for $C_{12}H_{13}O_2^+$ $(M+H)^+$: 189.0910, found 189.0907. GCMS (m/z): 188.08.

*1-Methoxy-4-(pent-4-yn-2-yl)benzene (**1h**).* **1h** was prepared in 82% (1.43 g) yield through the General Procedure A by using $BF_3{\cdot}OEt_2$ instead of the TFA. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.13 (m, 2H), 6.93–6.82 (m, 2H), 3.81 (s, 3H), 3.09–2.84 (m, 1H), 2.57–2.28 (m, 2H), 1.99 (t, J = 2.6 Hz, 1H), 1.47–1.31 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 137.7, 127.7, 113.8, 83.2, 69.4, 55.2, 38.0, 27.8, 20.9. HRMS (ESI) m/z calcd for $C_{12}H_{15}O^+$ $(M+H)^+$: 175.1117, found 175.1118. GCMS (m/z): 174.10

*6-Methoxy-1-(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalene (**1i**).* **1i** was prepared in 82% yield (1.64 g) through the General Procedure A by using $BF_3{\cdot}OEt_2$ instead of the TFA. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, J = 8.5 Hz, 1H), 6.70 (ddd, J = 14.4, 8.4, 2.6 Hz, 1H), 6.61 (d, J = 2.5 Hz, 1H), 3.78 (s, 3H), 3.04–2.90 (m, 1H), 2.87–2.65 (m, 2H), 2.62–2.50 (m, 1H), 2.50–2.35 (m, 1H), 2.01 (t, J = 2.6 Hz, 1H), 1.96–1.90 (m, 2H), 1.86–1.71 (m, 2H). HRMS (ESI) calcd for $C_{14}H_{17}O^+$ $(M+H)^+$: 201.1274, found 201.1274.

*1-(But-3-yn-1-yl)naphthalene (**1j**).* **1j** is a known compound.[21,22] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.56–7.45 (m, 2H), 7.45–7.34 (m, 2H), 3.34 (t, J = 7.7 Hz, 2H), 2.64 (td, J = 7.8, 2.6 Hz, 2H), 2.03 (t, J = 2.6 Hz, 1H).

*1-(But-3-yn-1-yl)-4-methoxynaphthalene (**1k**).* **1k** was prepared in 82% (1.73 g) yield through the General Procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (dd, J = 8.3, 0.9 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.52 (dddd, J = 24.4, 8.1, 6.8, 1.3 Hz, 2H), 7.28 (d, J = 7.8 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 3.97 (s, 3H), 3.27 (t, J = 7.7 Hz, 2H), 2.66–2.57 (m, 2H), 2.06 (t, J = 2.6 Hz, 1H). HRMS $(M+H)^+$ calcd for $C_{15}H_{15}O^+$: 211.1117, found 211.1120.

*2-Ethynyl-4′-methoxy-1,1′-biphenyl (**1ab**).* **1ab** is a known compound.[23] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.7, 0.9 Hz, 1H), 7.56–7.49 (m, 2H), 7.42–7.33 (m, 2H), 7.29–7.26 (m, 1H), 7.00–6.93 (m, 2H), 3.86 (s, 3H), 3.05 (s, 1H).

*4′-Chloro-2-ethynyl-1,1′-biphenyl (**1ac**).* **1ac** is a known compound.[24] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 2.2 Hz, 1H), 7.57–7.52 (m, 2H), 7.46–7.41 (m, 2H), 7.40–7.36 (m, 2H), 7.33–7.28 (m, 1H), 3.07 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 139.2, 133.4, 132.8, 130.8, 129.2, 129.1, 128.1, 127.9, 122.1, 81.8, 81.2.

*2-Ethynyl-4′-fluoro-1,1′-biphenyl (**1ad**).* **1ad** is a known compound.[23] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73–7.66 (m, 1H), 7.66–7.58 (m, 2H), 7.48–7.32 (m, 3H), 7.23–7.12 (m, 2H), 3.11 (d, J = 2.4 Hz, 1H).

*2-Ethynyl-3′-methyl-1,1′-biphenyl (**1ae**).* **1ae** was prepared in 82% yield (1.58 g) through the General Procedure B. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 7.5 Hz, 1H), 7.39 (ddd, J = 11.1, 9.3, 5.3 Hz, 4H), 7.31 (ddd, J = 10.7, 8.8, 4.7 Hz, 2H), 7.20 (d, J = 7.5 Hz, 1H), 3.05 (s, 1H), 2.43 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 140.2, 137.6, 133.9, 130.0, 129.6, 129.0, 128.3, 127.9, 126.9, 126.4, 120.5, 83.2, 80.1, 21.5. HRMS $(M+H)^+$ calcd for $C_{15}H_{13}^+$: 193.1012, found 193.1010.

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J. Org. Chem. 2017, 82, 7070–7076

*2-Ethynyl-5-fluoro-1,1′-biphenyl (**1af**).* **1af** is a known compound.[23] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.55 (m, 3H), 7.49−7.37 (m, 3H), 7.13−7.08 (m, 1H), 7.02 (td, J = 8.3, 2.7 Hz, 1H), 3.01 (s, 1H).

*2-(2-Ethynylphenyl)benzo[b]thiophene (**1ag**).* **1ag** is a known compound.[23] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89−7.84 (m, 2H), 7.84−7.80 (m, 1H), 7.66 (dd, J = 7.7, 1.2 Hz, 1H), 7.62 (dd, J = 7.9, 0.8 Hz, 1H), 7.42 (td, J = 7.7, 1.4 Hz, 1H), 7.40−7.34 (m, 2H), 7.34−7.29 (m, 1H), 3.30 (s, 1H).

General Procedure C. Gold catalyzed oxidation functionalization of terminal alkyne to dihydronaphthalen-2(1*H*)-ones **3** and phenanthrenols **5**. To a dram vial containing 2 mL of DCE was added sequentially the alkyne **1** (0.1 mmol), 2, 6-dichloropyridine 1-oxide **2a** (20 mg, 0.12 mmol, 1.2 equiv), TMe^{t}BuXPhosAuCl (1.4 mg, 0.002 mmol), and $NaBAr^F{}_4$ (2.6 mg, 0.003 mmol). The resulting mixture was stirred at 50 °C, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired dihydronaphthalen-2(1*H*)-ones **3** and phenanthrenols **5**.

*3,4-Dihydronaphthalen-2(1H)-one (**3a**).* **3a** is a known compound[25] and was prepared in 83% yield (12.1 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.25 (m, 3H), 7.18 (dd, J = 7.8, 4.1 Hz, 1H), 3.64 (s, 2H), 3.12 (t, J = 6.7 Hz, 2H), 2.66−2.56 (m, 2H).

*7-Methoxy-3,4-dihydronaphthalen-2(1H)-one (**3b**).* **3b** is a known compound[26] and was prepared in 98% (17.3 mg) yield according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.25 (m, 3H), 7.18 (dd, J = 7.8, 4.1 Hz, 1H), 3.64 (s, 2H), 3.12 (t, J = 6.7 Hz, 2H), 2.66−2.56 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 158.6, 134.5, 128.8, 128.6, 113.6, 112.4, 55.4, 45.2, 38.6, 27.5.

*7-(Benzyloxy)-3,4-dihydronaphthalen-2(1H)-one (**3c**).* **3c** is a known compound[27] and was prepared in 90% yield (22.7 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.28 (m, 5H), 7.14 (t, J = 6.2 Hz, 1H), 6.84 (dd, J = 8.3, 2.6 Hz, 1H), 6.76 (d, J = 2.5 Hz, 1H), 5.05 (s, 2H), 3.55 (s, 2H), 3.01 (t, J = 6.7 Hz, 2H), 2.57−2.51 (m, 2H).

*7-(Allyloxy)-3,4-dihydronaphthalen-2(1H)-one (**3d**).* **3d** was prepared in 79% yield (16.0 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, J = 8.3 Hz, 1H), 6.77 (dd, J = 8.3, 2.6 Hz, 1H), 6.69 (d, J = 2.5 Hz, 1H), 6.04 (ddt, J = 17.2, 10.5, 5.3 Hz, 1H), 5.40 (dq, J = 17.3, 1.6 Hz, 1H), 5.33−5.24 (m, 1H), 4.52 (dt, J = 5.3, 1.5 Hz, 2H), 3.54 (s, 2H), 3.00 (t, J = 6.7 Hz, 2H), 2.56−2.51 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 157.6, 134.5, 133.3, 129.0, 128.6, 117.7, 114.5, 113.2, 69.0, 45.2, 38.6, 27.5. HRMS (M+H)$^+$ calcd for $C_{13}H_{15}O_2^+$: 203.1067, found 203.1069.

*6,7-Dimethoxy-3,4-dihydronaphthalen-2(1H)-one (**3e**).* **3e** is a known compound[28] and was prepared in 62% yield (12.8 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (s, 1H), 6.62 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.52 (s, 2H), 3.00 (t, J = 6.7 Hz, 2H), 2.56 (t, J = 6.7 Hz, 2H).

*6,7,8-Trimethoxy-3,4-dihydronaphthalen-2(1H)-one (**3f**).* **3f** is a known compound[20] and was prepared in 98% yield (23.1 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.55 (s, 1H), 3.89−3.81 (m, 9H), 3.50 (s, 2H), 3.00 (t, J = 6.7 Hz, 2H), 2.61−2.49 (m, 2H).

*7-oxo-5,6,7,8-Tetrahydronaphthalen-2-yl acetate (**3g**).* **3g** was prepared in 53% yield (10.8 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.1 Hz, 1H), 6.93 (dd, J = 8.2, 2.4 Hz, 1H), 6.87 (d, J = 2.1 Hz, 1H), 3.57 (s, 2H), 3.05 (t, J = 6.7 Hz, 2H), 2.59−2.53 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 169.6, 149.4, 134.7, 134.3, 128.6, 121.3, 120.0, 44.9, 38.1, 27.8, 21.1. HRMS (ESI) m/z calcd for $C_{12}H_{13}O_3^+$ (M+H)$^+$: 205.0859, found 205.0859. GCMS (m/z): 204.08.

*7-Methoxy-4-methyl-3,4-dihydronaphthalen-2(1H)-one (**3h**).* **3h** was prepared in 70% yield (13.3 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J = 8.4 Hz, 1H), 6.80 (dd, J = 8.4, 2.6 Hz, 1H), 6.66 (d, J = 2.6 Hz, 1H), 3.79 (s, 3H), 3.57 (dt, J = 13.9, 12.4 Hz, 2H), 3.28−3.15 (m, 1H), 2.74−2.64 (m, 1H), 2.31 (dd, J = 16.4, 7.5 Hz, 1H), 1.31 (d, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.2, 158.5, 134.1, 133.4, 127.0, 113.6, 112.5, 55.4, 46.7, 44.8, 32.8, 20.4. HRMS (M+H)$^+$ calcd for $C_{12}H_{15}O_2^+$: 191.1067, found 191.1071.

*8-Methoxy-3a,4,5,6-tetrahydro-1H-phenalen-2(3H)-one (**3i**).* **3i** was prepared in 86% yield (18.6 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.25 (m, 3H), 7.18 (dd, J = 7.8, 4.1 Hz, 1H), 3.64 (s, 2H), 3.12 (t, J = 6.7 Hz, 2H), 2.66−2.56 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.4, 158.2, 137.8, 134.6, 128.4, 112.4, 111.5, 55.3, 46.0, 46.0, 33.2, 30.6, 29.9, 22.5. HRMS (M+H)$^+$ calcd for $C_{14}H_{17}O_2^+$: 217.1223, found 217.1223.

*3,4-Dihydrophenanthren-2(1H)-one (**3j**).* **3j** is a known compound[29] and was prepared in 94% yield (18.4 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.7, 5.2 Hz, 1H), 7.87 (t, J = 9.1 Hz, 1H), 7.73 (dd, J = 9.8, 5.2 Hz, 1H), 7.59−7.53 (m, 1H), 7.53−7.47 (m, 1H), 7.22 (d, J = 8.4 Hz, 1H), 3.75 (s, 2H), 3.51 (t, J = 6.8 Hz, 2H), 2.78−2.65 (m, 2H).

*9-Methoxy-3,4-dihydrophenanthren-2(1H)-one (**3k**).* **3k** is a known compound[30] and was prepared in 96% yield (21.7 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.62 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.54 (dd, J = 11.2, 4.0 Hz, 1H), 6.57 (s, 1H), 4.04 (d, J = 5.1 Hz, 3H), 3.77 (s, 2H), 3.47 (t, J = 6.8 Hz, 2H), 2.82−2.71 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 154.6, 132.2, 130.8, 127.1, 124.9, 124.8, 123.2, 122.8, 122.6, 104.5, 55.6, 45.1, 38.7, 24.0.

*Phenanthren-9-ol (**5aa**).* **5aa** is a known compound[31] and was prepared in 95% yield (18.4 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.25 (m, 3H), 7.18 (dd, J = 7.8, 4.1 Hz, 1H), 3.64 (s, 2H), 3.12 (t, J = 6.7 Hz, 2H), 2.66−2.56 (m, 2H).

*2-Methoxyphenanthren-9-ol (**5ab**).* **5ab** is a known compound[32] was prepared in 99% yield (22.2 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (t, J = 8.4 Hz, 1H), 8.48 (d, J = 9.0 Hz, 1H), 8.27 (dd, J = 8.1, 1.0 Hz, 1H), 7.71−7.61 (m, 1H), 7.57 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.16−7.10 (m, 1H), 7.10−7.05 (m, 1H), 6.95 (s, 1H), 5.81−5.33 (m, 1H), 3.92 (d, J = 18.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 150.2, 134.2, 131.7, 127.3, 125.4, 124.5, 124.2, 122.3, 122.2, 121.1, 114.5, 107.3, 106.0, 55.4.

*2-Chlorophenanthren-9-ol (**5ac**).* **5ac** is a known compound[33] and was prepared in 94% yield (21.4 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, J = 8.9 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 2.3 Hz, 1H), 7.76−7.71 (m, 1H), 7.70−7.64 (m, 1H), 7.62−7.52 (m, 2H), 7.31 (s, 1H), 7.07 (s, 1H), 5.60 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 132.6, 132.6, 129.9, 127.7, 127.2, 126.9, 126.7, 126.3, 124.7, 124.4, 122.5, 122.1, 107.2.

*2-Fluorophenanthren-9-ol (**5ad**).* **5ad** was prepared in 74% yield (15.7 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62−8.52 (m, 2H), 8.31 (dd, J = 8.1, 1.0 Hz, 1H), 7.70 (ddd, J = 8.3, 5.5, 1.4 Hz, 1H), 7.64 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 7.33 (dd, J = 9.7, 2.7 Hz, 1H), 7.23 (ddd, J = 9.0, 8.5, 2.7 Hz, 1H), 6.95 (s, 1H), 5.52 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7, 160.8, 150.6, 134.2 (d, J_{F-C} = 9.2 Hz), 131.4, 127.6, 126.2, 125.0, 124.8 (d, J_{F-C} = 9.1 Hz), 123.3 (d, J_{F-C} = 1.8 Hz), 122.5, 113.0 (d, J_{F-C} = 23.7 Hz), 110.8 (d, J_{F-C} = 21.2 Hz), 105.5 (d, J_{F-C} = 3.6 Hz). HRMS (ESI) m/z calcd for $C_{14}H_{10}FO^+$ (M+H)$^+$ 213.0710, found 213.0706.

*4-Methylphenanthren-9-ol (**5ae**):1-Methylphenanthren-9-ol (**5ae′**).* **5ae**:**5ae′** is a known compound[34] and was prepared in 71% yield (14.8 mg) according to the General Procedure C. **5ae**:**5ae′** = 1:2, In this ^{1}HNMR, **5ae** is 1, **5ae′** is 2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 8.3 Hz, 1H), 8.67 (d, J = 8.2 Hz, 2H), 8.35−8.26 (m, 3H), 7.74−7.57 (m, 8H), 7.40 (dd, J = 6.5, 3.6 Hz, 2H), 7.37 (dt, J = 7.4, 3.7 Hz, 2H), 7.21 (s, 1H), 6.99 (s, 2H), 5.71−4.77 (m, 4H), 2.66 (s, 3H), 2.59 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 148.8, 135.8, 133.8, 132.8, 131.9, 131.5, 131.2, 130.8, 130.4, 129.4, 128.6, 128.0, 127.2, 127.0, 126.8, 126.6, 126.6, 126.2, 125.7, 125.1, 124.5, 123.8, 123.0, 122.7, 122.4, 122.3, 122.2, 120.7, 106.0, 102.7, 21.9, 20.0.

*6-Fluorophenanthren-9-ol (**5af**).* **5af** was prepared in 75% yield (15.9 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, J = 8.2 Hz, 1H), 8.32 (dd, J = 9.0, 6.0 Hz,

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J. Org. Chem. 2017, 82, 7070−7076

1H), 8.26 (dd, J = 11.1, 2.5 Hz, 1H), 7.72−7.67 (m, 1H), 7.55 (tt, J = 5.5, 2.7 Hz, 1H), 7.49 (ddd, J = 13.5, 7.5, 4.0 Hz, 1H), 7.38 (ddd, J = 8.9, 8.1, 2.5 Hz, 1H), 6.96 (s, 1H), 5.37 (d, J = 72.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 161.2, 149.4, 133.3, 127.6, 126.8, 126.2 (d, J_{F-C} = 4.0 Hz), 125.0 (d, J_{F-C} = 9.0 Hz), 124.3, 122.8, 122.3 (d, J_{F-C} = 1.5 Hz), 115.3 (d, J_{F-C} = 23.8 Hz), 107.9 (d, J_{F-C} = 22.5 Hz), 105.3 (d, J J_{F-C} = 2.1 Hz). HRMS (ESI) m/z calcd for $C_{14}H_{10}FO^+$ $(M+H)^+$ 213.0710, found 213.0710.

*Benzo[b]naphtho[2,1-d]thiophen-5-ol (**5ag**).* **5ag** was prepared in 92% yield (23.0 mg) according to the General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 8.3 Hz, 1H), 7.94−7.70 (m, 3H), 7.31−7.25 (m, 3H), 7.05−6.81 (m, 2H), 5.67(s,1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 139.6, 136.2, 131.4, 130.5, 130.1, 128.5, 126.6, 126.0, 124.8, 124.6, 124.4, 123.6, 123.2, 122.8, 107.9. HRMS $(M+H)^+$ calcd for $C_{16}H_{11}OS^+$: 251.0525, found 251.0533.

General Procedure D. Gold catalyzed functionalization of terminal alkynes anti-Markovnikov's rule to 1,2-dihydronaphthalene **4e** and **4f**.

To a dram vial containing 2 mL of DCE was added sequentially the alkyne **1** (0.1 mmol), TMe^{t}BuXPhosAuCl (1.4 mg, 0.002 mmol), and $NaBAr^F{}_4$ (2.6 mg, 0.003 mmol). The resulting mixture was stirred at appropriate temperature, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent:hexanes/ethyl acetate) to afford the desired 1,2-dihydronaphthalene **4e** and **4f**.

*6,7-Dimethoxy-1,2-dihydronaphthalene (**4e**).* **4e** is a known compound[28] and was prepared in 75% yield (14.3 mg) according to the General Procedure D at 60 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.66 (s, 1H), 6.60 (s, 1H), 6.38 (d, J = 9.6 Hz, 1H), 5.99−5.87 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.73 (t, J = 8.3 Hz, 2H), 2.29 (tdd, J = 8.1, 4.4, 1.8 Hz, 2H).

*5,6,7-Trimethoxy-1,2-dihydronaphthalene (**4f**).* **4f** is a known compound[35] and was prepared in 69% yield (15.2 mg) according to the General Procedure D at 40 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (dt, J = 9.8, 1.7 Hz, 1H), 6.52 (s, 1H), 5.99 (dt, J = 9.7, 4.4 Hz, 1H), 3.95−3.84 (m, 10H), 2.75 (dd, J = 12.4, 4.6 Hz, 2H), 2.31 (tdd, J = 8.0, 4.4, 1.8 Hz, 2H).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01244.

Detailed experimental procedures and ^{1}H, ^{13}C, and HRMS data (PDF)

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Notes

The authors declare no competing financial interest.

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